The corrected mean heat of combustion of titanium nitride is 2337.3$_6$ cal. per gram for the sample burning at constant volume and in an initial oxygen pressure of 30 atm. The corresponding value for titanium carbide is 4590.8$_1$ cal. per gram. Molecular weights, computed from the 1949 Table of International Atomic Weights, were used to obtain, from the heats of combustion per gram, the values of the energy changes in the bomb ($-\Delta U_B$) for the combustion of one mole of titanium nitride, or carbide, to titanium dioxide (rutile) and nitrogen, or carbon dioxide.

To obtain the heats of combustion under standard conditions ($-\Delta H_R$), the value obtained for $-\Delta U_B$ must be corrected (1) to unit fugacity, (2) to a constant-pressure process and (3) to standard temperature. The values used for the intrinsic energy change of the gases with pressure were oxygen,[10] -1.56, nitrogen,[10] -1.43 and carbon dioxide,[11] -6.72 cal. per atm. per mole at 30°. The relation $\Delta H = \Delta U + RT\Delta n$ was used to compute the correction for the constant-pressure process, and values for computing ΔC_p to correct to standard temperature were taken from Kelley.[12]

The standard heats of combustion ($-\Delta H_R$) of titanium nitride and carbide are listed in Table II, together with the heats of combustion obtained under bomb conditions ($-\Delta U_B$), the standard heats of formation from the elements ($-\Delta H_f^0$), and the standard free energies of formation ($-\Delta F_f^0$). The deviations listed are the uncertainty interval of Rossini[13] and include, in addition to the respective precision errors taken for the heat of combustion of benzoic acid, the calibration experiments, and the combustion experiments on the nitride and carbide, reasonable values assigned to the possible errors in the corrections for impurities and incomplete combustion. In computing standard heats of formation, the value 225.5$_2$ ± 0.2$_3$ kcal./mole, obtained earlier[5] for the combustion of titanium metal to titanium dioxide, was used, as well as the value, 94,051.8 ± 10.8 cal./mole, for the heat of formation of carbon dioxide.[14] The entropy values listed by Kelley[12] were used to obtain the free energies of formation.

TABLE II

SUMMARY OF DERIVED DATA FOR TITANIUM NITRIDE AND TITANIUM CARBIDE[a]

Compound	$-\Delta U_B$ kcal./mole at 30°	$-\Delta H_R$ kcal./mole at 25°	$-\Delta H_f^0$ kcal./mole at 25°	$-\Delta F_f^0$ kcal./mole at 25°
TiN	$144.7_0 \pm 0.1_4$	$145.0_5 \pm 0.1_4$	$80.4_7 \pm 0.2_7$	$73.6_5 \pm 0.2_7$
TiC	$275.0_4 \pm .3_2$	$275.7_2 \pm .3_2$	$43.8_5 \pm .3_9$	$43.0_1 \pm .3_9$

[a] Errors are "uncertainty interval."

The value found here for the heat of formation of titanium nitride is in good agreement with that of Neumann.[4] Comparison with free energy values listed by Kelley[15] and Brewer, *et al.*,[16] indicates that titanium carbide and nitride are among the thermodynamically most stable carbides and nitrides.

(10) F. D. Rossini and M. Frandsen, *J. Research Natl. Bur. Standards*, **9**, 733 (1932).

(11) E. W. Washburn, *ibid.*, **10**, 525 (1933).

(12) K. K. Kelley, *Bur. Mines Bull.*, 477 (1949).

(13) F. D. Rossini, *Chem. Rev.*, **18**, 233 (1936).

(14) E. J. Prosen, R. S. Jessup and F. D. Rossini, *J. Research Nat. Bur. Standards*, **33**, 447 (1944).

(15) K. K. Kelley, Bur. Mines Bull. 407 (1938).

(16) L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, "Chemistry and Metallurgy of Miscellaneous Materials," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, pp. 40-59.

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The Inductive Effect and Chemical Reactivity. I. General Theory of the Inductive Effect and Application to Electric Dipole Moments of Haloalkanes

BY RICHARD P. SMITH, TAIKYUE REE, JOHN L. MAGEE[1] AND HENRY EYRING

The inductive effect is discussed qualitatively in terms of bond orbital theory, and the main features of the effect are pointed out. A simple semi-classical model for the inductive effect is then introduced, and the analysis of this model leads to a method for calculating approximately net charges on atoms in molecules having no conjugation. All of the parameters are obtained from accepted longitudinal polarizabilities, screening constants, covalent bond radii and electric dipole moments. The method is checked by comparing calculated and observed electric dipole moments of some halogen substituted alkanes, and excellent agreement is found. The method will be shown, in succeeding papers, to be of great utility in understanding relative organic reaction rates and equilibria.

Introduction

The inductive effect has long been recognized as playing a prominent role in determining relative rates of organic reactions. The extent of this role has heretofore been impossible to determine, inasmuch as steric and resonance effects often overshadow—or have been thought to overshadow—the inductive effect, and lack of understanding of the nature of the effect has prohibited the calculation of its magnitude.

The successful correlation of relative amounts of ortho, meta and para nitration of substituted benzenes with empirically calculated charges[2] indicates that rough calculations of charges can be useful for discussing chemical reactivity semi-quantitatively. In this paper we propose to develop a general, approximate theory for calculating the magnitudes of charges on atoms in molecules having no conjugation. The theory will be checked by comparing a number of calculated and observed dipole moments. Succeeding papers in this series will show how reaction rates and equilibria may be semi-quantitatively correlated with charges calculated on the basis of our model for the inductive effect and improvements on it.

The principal inductive effect theories in existence are those of Branch and Calvin[3] and

(1) Department of Chemistry, University of Notre Dame, Notre Dame, Ind.

(2) T. Ri (Ree) and H. Eyring, *J. Chem. Phys.*, **8**, 433 (1940).

(3) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, pp. 217ff.

Remick.[4] Branch and Calvin followed ideas similar to those of Ingold and collaborators,[5] who suppose that substituent effects are propagated principally along chemical bonds in molecules. Using the observations of Derick[6] and others, they developed an empirical method for calculating acid strengths. "Inductive constants" were assigned to various groups, and rules for their application were given. A number of acid strengths were calculated on the basis of this theory, and rough accord with experiment was obtained. The theory of Remick is less empirical, being based largely on electronic polarizations of bonds and changes in effective kernel charges; it was used for discussing the dipole moments of some polyhalogeno alkanes. This theory bears some resemblance to the theory which we shall develop here; a further discussion of Remick's theory and its relationship to ours will be given later in this paper.

The problem of charge distribution in molecules is of course a quantum mechanical problem; consequently we shall first discuss the inductive effect quantum mechanically. This will lead to a simple picture for the inductive effect, but the approximations necessary for the development of a general theory will not permit its actual numerical application. Consequently, we shall use a semi-classical model, and thereby develop a simple method for calculating charge distributions; the results of the application of this method will, we believe, amply justify its use.

Bond Orbital Treatment of the Inductive Effect

We now discuss the inductive effect quantum mechanically, considering the electron pair of each bond as moving in a molecular orbital which may be written as a linear combination of atomic orbitals (L.C.A.O.) of the two atoms between which the electrons move. This localized electron pair, L.C.A.O. model seems necessary for simplicity in developing a general theory which readily permits approximate identification of net charges associated with individual atoms. Thus in the convenient notation of Mulliken,[7] we write

$$\varphi_B = a_B\chi_a + b_B\chi_b \qquad (1)$$

for the bonding (lower energy) orbital in which the two electrons of a bond a–b are supposed to move. Here χ_a and χ_b are the atomic orbitals and a_B and b_B are numerical coefficients obtained by normalization of (1) and minimization of the energy with respect to the coefficients. When the coefficients are thus obtained and inserted into the expressions

$$Q_a = Q = -2e(a_B{}^2 + a_Bb_BS) + e \qquad (2)$$

and

$$Q_b = -Q = -2e(a_Bb_BS + b_B{}^2) + e \qquad (3)$$

for the approximate net charges on atoms a and b, respectively, it is found[7] that

$$Q = (\delta/\beta)[1 - {}^1/_2(1 - S^2)(\delta^2/\beta^2) + \ldots] \qquad (4)$$

where

$$\delta = {}^1/_2(\alpha_b - \alpha_a),\ \alpha_a = \int\chi_a{}^*h\chi_a d\tau,\ \alpha_b = \int\chi_b{}^*h\chi_b d\tau,$$
$$\beta = \gamma - {}^1/_2S(\alpha_a + \alpha_b),\ \gamma = \int\chi_a{}^*h\chi_b d\tau,\ S = \int\chi_a{}^*\chi_b d\tau$$

where h is the S.C.F. (self consistent field) one-electron Hamiltonian. In general it should be a satisfactory approximation to drop all terms in (4) but the first. Now Mulliken finds that the integral β is remarkably invariant with respect to a number of factors, including the polarity of the bond.[7] Hence Q should be approximately linear in δ, which for bonds of the type we are considering has been shown by Mulliken to be given approximately by

$$\delta = {}^1/_2A[(I_a - {}^1/_2J_{aa}) - (I_b - {}^1/_2J_{bb})] \qquad (5)$$

Here I_a and I_b are the ionization potentials for atoms a and b, respectively, in the appropriate valence states; A is roughly constant, being about 0.5 for the bonds studied by Mulliken; and J_{aa} and J_{bb} are integrals defined by

$$J_{ii} = \int\chi_i{}^{*(1)}\chi_i\frac{e^2}{r_{12}}\chi_i{}^{*(2)}\chi_i{}^{(2)}d\tau_1\,d\tau_2 \qquad (6)$$

where the subscripts and superscripts (1) and (2) refer to the individual electrons of the bond.

Substitution of (5) into (4), neglecting higher order terms, gives

$$Q = Q_a = {}^1/_2|\beta^{-1}|A[(I_b - {}^1/_2J_{bb}) - (I_a - {}^1/_2J_{aa})] \qquad (7)$$

since β is negative. Equation (7) permits us to see, qualitatively, the nature of the inductive effect. The quantity I_b is positive and roughly proportional to the square of the effective nuclear charge of atom b, while J_{bb} is positive and roughly proportional to the nuclear charge of b. Similar statements apply to I_a and J_{aa}. Suppose a substituent removes charge from b. This will increase the effective nuclear charge of b, and therefore $(I_b - {}^1/_2J_{bb})$, since I_b predominates over ${}^1/_2J_{bb}$. Hence Q increases, *i.e.*, electrons are pulled from a onto b; the resulting increase of the effective nuclear charge of a will cause a to pull electrons from the other atoms to which it is attached, and so on. The approximations made in the derivation of (7), together with the uncertainties in the quantities in the right-hand side of this equation, prevent us, at present, from actually using this formulation of the theory for numerical calculations.

"Semi-classical" Treatment of the Inductive Effect

We now proceed to develop the theory of the inductive effect on the basis of a simple model. Although the model used is probably only a rough approximation to the situation, its use permits calculation of the parameters involved in terms of quantities whose values are known empirically, and the numerical results obtained are surprisingly good.

The moment μ induced in a system by a field of strength E is

$$\mu = \alpha E \qquad (8)$$

where α is the polarizability tensor; the non-diagonal components of α will vanish if the axes of the system are properly chosen. An approximation frequently used for chemical bonds is the assumption that the diagonalized polarizability tensor has one component b_l and two components b_t where b_l is the "longitudinal polarizability," *i.e.*, the polarizability in the direction of the bond, and where b_t is the "transverse polarizability" which is perpendicular to the bond direction. This assumption

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[4] A. E. Remick, *J. Chem. Phys.*, **9**, 653 (1941).

[5] C. K. Ingold, *Chem. Rev.*, **15**, 225 (1934).

[6] C. G. Derick, THIS JOURNAL, **33**, 1152 (1911).

[7] R. S. Mulliken, *Colloques intern. centre natl. recherche sci.*, No. **18**, *Liaison chim.*, **1948**, 158 (1950); *J. chim. phys.*, **46**, 497 (1949).

has been discussed and applied by Wang[8] and by Denbigh.[9]

Let us now consider the application of the bond-direction component of (8) to the electron cloud of the two bonding electrons of a bond *a–b*. It seems reasonable to write

$$-Q_a{}^bR_{ab} = (b_l)_{ab}\left(\frac{z_a e}{R_a 2} - \frac{z_b e}{R_b 2}\right) \tag{9}$$

where $Q_a{}^b$ is the net charge on atom *a* due to the polarization of the electron pair of *a–b*, R_{ab} is the internuclear distance and $(b_l)_{ab}$ the longitudinal polarizability of *a–b*, z_a and z_b are the effective nuclear charges of *a* and *b*, respectively, in the molecule, and R_a and R_b are the covalent bond radii of *a* and *b*, respectively. The minus sign was introduced for consistency between the direction of the field and the induced moment. The principal assumptions embodied in (9) are (a) that a bond dipole moment may be represented by equal and opposite net charges localized on the atomic nuclei, and (b) that the dipoles are induced by a net force of the form represented in (9). Assumption (a) seems necessary in any simple treatment of the inductive effect. Assumption (b) amounts to assuming spherical potential fields for atoms *a* and *b*, neglecting asymmetry due to the fact that the bonding electrons have a greater probability of being found between the atoms than elsewhere, and that the conducting spheres on which the electrons move have, on the average, radii equal to the covalent bond radii.

According to Slater,[10] one electron on atom *a* exerts a screening of s_a on another in the same valence shell, where s_a is 0.35 unless the electron is in the *ls* group, in which case 0.30 is used; hence we write

$$z_a = z_a{}^0 + \frac{s_a}{e}\epsilon_a \tag{10}$$

where $z_a{}^0$ is a constant for atom *a*, and ϵ_a is the *total* net charge on this atom (sum of net charge contributions from all bonds joined to *a*). Substitution of (10) and a similar equation for z_b into (9) yields

$$Q_a{}^b = \alpha_{ab} + \beta_b{}^a\epsilon_b - \beta_a{}^b\epsilon_a \tag{11}$$

where

$$\alpha_{ab} = -\frac{(b_e)_{ab}\,e}{R_{ab}}\left[\frac{Z_a{}^0}{R_a{}^2} - \frac{Z_b{}^0}{R_b{}^2}\right] \tag{12}$$

$$\beta_b{}^a = \frac{S_b(b_e)_{ab}}{R_{ab}R_b{}^2} \qquad \beta_a{}^b = \frac{S_a(b_e)_{ab}}{R_{ab}R_a{}^2} \tag{13}$$

It is of interest to note, at this point, the relationship of the theory of Remick[4] to ours. Remick considered only C–C bonds and C–X bonds where X was hydrogen or halogen. For the carbon–halogen bonds Remick derived the equation

$$\bar{\mu}_{cx} - \bar{\mu}^0{}_{cx} = -1.583 \times 10^{-24}(P_E{}')_{cx}\ \Delta q_c{}^{\#}/R^2{}_{cx}$$

where $\bar{\mu}^0{}_{cx}$ is a "standard bond moment," $\bar{\mu}_{cx}$ is the moment under the influence of a change $\Delta q_c{}^{\#}$ in the effective kernel charge of the carbon, R_{CX} is the C–X bond length, and $(P_E{}')_{CX}$ is the electronic polarization of the electron pair of C–X. Using the relations

$$\frac{4\pi N}{3}\alpha = P_E{}' \qquad \frac{b_l + 2b_t}{3} = \alpha$$

and the following relation, found empirically by Denbigh[9] for carbon–halogen bonds

$$b_t = 0.57b_l$$

Remick's equation reduces to

$$\bar{\mu}_{cx} - \bar{\mu}^0{}_{cx} = -2.95(b_l)_{cx}\frac{\Delta q_c{}^{\#}}{R^2{}_{cx}}$$

If we make the approximation $R_C \approx R_X \approx {}^1/_2R_{CX}$, our theory gives us the corresponding equation

$$\delta\mu_{cx} = -4(b_l)_{cx}\frac{Z_c{}'e}{R^2{}_{cx}}$$

for the change, $\delta\mu_{cx}$, in the C–X moment due to a change $z_C{}'$ in the effective charge of the carbon. We use $z_C{}'e = 0.35\ \epsilon_c{}'$, where $\epsilon_c{}'$ is the change in electronic charge on the carbon, the factor 0.35 naturally arising from Slater's screening rules, while Remick empirically uses $\Delta q_c{}^{\#} = {}^1/_3\ \epsilon_c{}'$. Similar considerations apply to the other bonds discussed by Remick. Thus our theory has much in common with Remick's, although we believe ours to be a more *direct* theory, being based on a simpler model, and not requiring empirical corrections as did the former theory.

The α_{ab} defined by (12) depend on small differences between large quantities, and are therefore very sensitive to the values of the $z_i{}^0$ and the R_i. In view of the uncertainties in these quantities, the α_{ab} are best determined from measured electric dipole moments, as will be explained later.

The $\beta_a{}^b$, on the other hand, present no such problem. It is found that our calculated charge distributions are sufficiently insensitive to small changes in the $\beta_a{}^b$ that the approximate values obtained in the following way are satisfactory. We use $R_{ab} = R_a + R_b$, and use Pauling's covalent bond radii[11] for the R_i. We use values of b_l from Denbigh.[9] The results for a number of bonds are summarized in Table I. Note that our theory from the field-polarizability viewpoint is immediately applicable to double bonds.

TABLE I

SOME CALCULATED VALUES OF $\beta_a{}^b$ AND $\beta_b{}^a$

Bond *a–b*	$b_l \times 10^{24}$, cc.	R_a, Å.	R_b, Å.	$\beta_a{}^b$	$\beta_b{}^a$
C–C	1.88	0.771	0.771	0.718	0.718
C–F	0.96[a]	.771	.64	.401	.581
C–Cl	3.67	.771	.99	1.23	.744
C–Br	5.04	.771	1.14	1.55	.710
C–I	8.09[a]	.771	1.33	2.27	.762
C–H	0.79	.771	0.30	0.434	2.46
C–O	.84[a]	.771	.66	.346	0.472
C–N	.86[a]	.771	.70	.344	.418
N–H	.58	.70	.30	.414	1.93
S–H	2.30	1.04	.30	.555	5.72
C═O	1.99	0.665	.55	1.30	1.90
C═C	2.86	.665	.665	1.70	1.70
C═S	7.57	.665	.94	3.73	1.87
N≡N	2.43	.547	.547	2.60	2.60
C≡N	3.1	.602	.547	2.61	3.16
C≡C	3.54	.602	.602	2.84	2.84
C_{ar}-C_{ar}[b]	2.25	.695[c]	.695[c]	1.17	1.17

[a] These values calculated assuming $b_t/b_l = 0.57$, a relationship Denbigh[9] found for C–Cl and C–Br bonds, and using bond refraction values given by Denbigh. [b] Nuclear bond in benzene and derivatives. [c] One-half carbon–carbon distance in benzene.

Application of the Theory to Organic Molecules

Basically, application of our charge distribution theory to a molecule involves the solution of simultaneous equations of the form of (11), one for each bond, subject to the restriction that the sum of the

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

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

[10] J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

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

net charges must be zero. In practice, it is apparent that there will in general be fewer equations to solve for a given molecule than there are bonds in the molecule, if use is made of obvious charge equalities—for example, each of the three hydrogens in CH_3X has the same net charge.

Let us now consider the application of the theory to some simple molecules with two purposes in mind: Illustration of the method of application, and determination of some of the parameters. First, let us make our notation more compact by introducing the quantities

$$\gamma_{ab} = \frac{\alpha_{ab}}{1 + \beta_a{}^b} \qquad \beta_{ab} = \frac{\beta_b{}^a}{1 + \beta_a{}^b} \tag{14}$$

Then if a is an atom which is attached *only* to a particular carbon atom (a = F, Cl, Br, I, H, O of O=C, etc.), and b is carbon, then $Q_a{}^b = \epsilon_a$ and (11) becomes, using definitions (14)

$$\epsilon_x = \gamma_{xc} + \beta_{xc}\epsilon_c \tag{15}$$

Using the $\beta_a{}^b$ of Table I, we find $\beta_{HC} = 0.13$, $\beta_{FC} = 0.25$, $\beta_{ClC} = 0.71$, $\beta_{BrC} = 0.91$, and $\beta_{IC} = 1.29$. For the molecules CH_3X, then, we have the equations

$$\epsilon_X = \gamma_{XC} + \beta_{XC}\epsilon_C \tag{16a}$$
$$\epsilon_H = \gamma_{HC} + \beta_{HC}\epsilon_C \tag{16b}$$

to be solved subject to the condition that

$$\epsilon_C + \epsilon_X + 3\epsilon_H = 0 \tag{16c}$$

The solution of the set of equations (16) is

$$\epsilon_H\Delta = (1 + \beta_{XC})\gamma_{HC} - \beta_{HC}\gamma_{XC} \tag{17a}$$
$$\epsilon_C\Delta = -\gamma_{XC} - 3\gamma_{HC} \tag{17b}$$
$$\epsilon_X\Delta = (1 + 3\beta_{HC})\gamma_{XC} - 3\beta_{XC}\gamma_{HC} \tag{17c}$$

where

$$\Delta = 1 + \beta_{XC} + 3\beta_{HC} \tag{17d}$$

Now the methyl halide bond angles are undoubtedly very close to tetrahedral[12,13]; assuming them to be tetrahedral, we have, for the methyl halide electric dipole moments

$$\mu_{CH_3X} = -\epsilon_X R_{CX} + \epsilon_H R_{CH} \tag{18}$$

where R_{CX} and R_{CH} are the C–X and C–H internuclear distances, respectively. Combining (18) with equations (17), we have

$$\mu_{CH_3}(1 + \beta_{XC} + 3\beta_{HC}) = \gamma_{HC}\,[3\beta_{XC}R_{CX} + (1 + \beta_{XC})R_{CH}] - \gamma_{XC}[(1 + 3\beta_{HC})R_{CX} + \beta_{HC}R_{CH}] \tag{19}$$

Equation (19) may be used to calculate the γ_{XC} for the carbon–halogen bonds from the parameters given previously, the measured internuclear distances,[12] the measured electric dipole moments as given in Table II, and γ_{HC}. The value of γ_{HC} may be determined from the moment of the C–H bond in methane as follows. In equations (17) if X is H (methane) we find $\epsilon_H = \gamma_{HC}/(1 + 4\beta_{HC})$ or $\gamma_{HC} = 1.52\,\epsilon_H$. Using 0.3 debye for the moment of the CH bond in methane[14,15,16] and 1.09 Å. as the length of this bond[11] we find, assuming a direction C^+H^-, that $\gamma_{HC} = -0.418 \times 10^{-10}$ e.s.u. There is some possibility that the CH bond moment is in the opposite direction[16]; in this case we find $\gamma_{HC} = 0.418 \times 10^{-10}$ e.s.u. for a moment of the same magnitude. In our calculations in this paper we have used both of the above values of γ_{HC} and also $\gamma_{HC} = 0$ corresponding to no C–H bond moment in methane.

The results of our calculations are summarized in Table II. We now have the values of all the parameters necessary for the calculation of charge distributions for all haloalkanes. The distributions may be tested by comparing the calculated and observed electric dipole moments; some results of such tests are summarized in Table II. The results for the series CH_3X, CH_2X_2, CHX_3 are shown graphically in Fig. 1. In these calculations, all bond angles have been assumed tetrahedral, and the bond distances have been assumed to be the same as in the corresponding methyl halides. The carbon–carbon distance has been taken as 1.54 Å.[11] Note, from its definition, that $\alpha_{CC} = 0$; hence application of (11) to the carbon–carbon bond in ethyl chloride, for example, yields

$$Q_2{}^1 = \beta_c{}^c\,(\epsilon_1 - \epsilon_2) \tag{20}$$

where $Q_2{}^1$ is the net charge contribution to carbon 2 of the carbon–carbon bond; the carbons are numbered 1, 2 starting from the substituent. We note that carbon 2, having three hydrogens substituted on it, each with charge ϵ_b, has the total net charge

$$\epsilon_2 = -3\epsilon_b + Q_2{}^1 \tag{21}$$

Hence, using (20)

$$\epsilon_2 + 3\epsilon_b = \beta_c{}^c\,(\epsilon_1 - \epsilon_2) \tag{22}$$

Hence for ethyl chloride the charge distribution is found by solving (22) simultaneously with

$$\epsilon_{Cl} = \gamma_{ClC} + \beta_{ClC}\,\epsilon_1 \tag{23}$$
$$\epsilon_a = \gamma_{HC} + \beta_{HC}\,\epsilon_1 \tag{24}$$
$$\epsilon_b = \gamma_{HC} + \beta_{HC}\,\epsilon_2 \tag{25}$$
$$\epsilon_1 + \epsilon_2 + 2\epsilon_a + 3\epsilon_b + \epsilon_{Cl} = 0 \tag{26}$$

where ϵ_a is the charge on each hydrogen attached

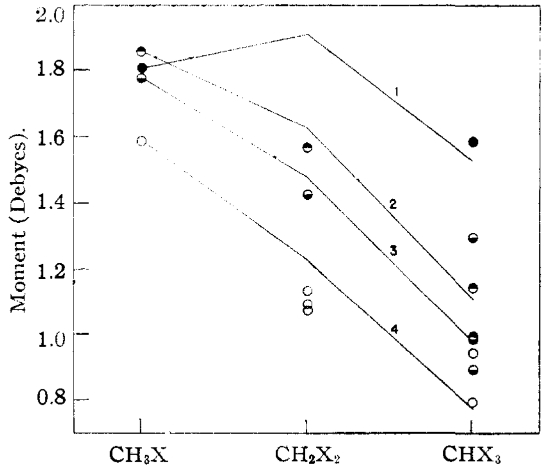

Fig. 1.—Calculated and observed moments for halogen substituted methanes. Lines are calculated, assuming no methane CH moment, and fitting experimental points for CH_3X molecules. Points are experimental. Lines 1, 2, 3 and 4, are for X = F, Cl, Br and I, respectively.

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(12) W. Gordy, J. W. Simmons and A. G. Smith, *Phys. Rev.*, **74**, 243 (1948).

(13) H. A. Skinner, *J. Chem. Phys.*, **16**, 553 (1948).

(14) R. Rollefson and R. Havens, *Phys. Rev.*, **57**, 710 (1940).

(15) C. A. Coulson, *Trans. Faraday Soc.*, **38**, 433 (1942).

(16) W. L. G. Gent, *Quarterly Reviews* (*London*), **2**, 383 (1948).

TABLE II

VALUES OF γ_{XC} FOR CX BONDS AND DIPOLE MOMENTS OF HALOALKANES

Molecule	$\gamma_{XC} \times 10^{10}$, e.s.u.			$\mu_{calcd.}$ (D)			$\mu_{obsd.}$ (D)[a]	Ref.
	C^-H^+	O	C^+H^-	C^-H^+	O	C^+H^-		
CH_3F	−0.944	−1.44	−1.93	(1.81	1.81	1.81)	1.81	17, 21
CH_2F_2				1.91	1.91	1.93	..	
CHF_3				1.51	1.53	1.54	1.59	19
CH_3Cl	−0.584	−1.49	−2.40	(1.86	1.86	1.86)	1.86	20
CH_2Cl_2				1.58	1.63	1.68	1.57	20
$CHCl_3$				1.04	1.12	1.19	1.01, 1.15	20, 22
CH_3Br	−0.354	−1.44	−2.53	(1.78	1.78	1.78)	1.78	17
CH_2Br_2				1.40	1.48	1.55	1.43	19
$CHBr_3$				0.88	0.98	1.08	1.3, 0.99, 0.90	18, 19, 22
CH_3I	0.081	−1.73	−2.82	(1.59	1.59	1.59)	1.59	17
CH_2I_2				1.12	1.23	1.34	1.10B, 1.08B, 1.14H	18
CHI_3				0.63	0.78	0.93	0.8B, 0.95B, 1.00H	18
$CFCl_3$				1.00	0.95	0.88	.45	21
CF_2Cl_2				1.23	1.18	1.12	.51	21
CCl_3Br				0.61	0.59	0.57		18
C_2H_5F				2.01	2.05	2.08	1.92	17
C_2H_5Cl				1.98	2.13	2.28	2.03	17
C_2H_5Br				1.85	2.05	2.25	2.02	17
C_2H_5I				1.57	1.86	2.15	1.90	17

[a] Gas values, if not otherwise indicated (B, benzene; H, hexane).

to carbon 1. Charge distributions for each haloalkanes are obtained similarly.

Discussion

Inspection of Table II reveals that the value of the methane C–H bond moment, which indirectly enters the calculations through γ_{HC}, does not make as much difference in the calculated dipole moments as might be expected. In fact, it is difficult to say which of the three "calculated" columns in Table II gives the best agreement with the observed values. As far as the four series CH_3X, CH_2X_2, CHX_3 are concerned it may be said that any of the three "calculated" columns gives satisfactory agreement with experiment, with the column corresponding to no CH moment probably giving the best agreement. For the ethyl halides the zero CH moment column represents the best agreement for ethyl bromide and ethyl iodide while the C^-H^+ column gives the best agreement for ethyl fluoride and ethyl chloride. The smallness of the moments of $CFCl_3$, CF_2Cl_2 and CCl_3Br as compared to all the calculated values can probably be attributed to a large extent to bond shortening and angle spreading in these molecules.

It is not to be concluded, however, that the CH bond in methane has no moment, particularly in view of the large amount of evidence supporting a moment.[16] The consistently high dipole moments calculated for a C^+H^- moment may be due to inaccuracies in the calculations from other sources, *e.g.*, the values we have used for the screening constants s_a may not be the "correct" values. Other inaccuracies are inherent in the theory, *e.g.*, the approximation that the electron distributions may be considered as point charges localized on nuclei as we have assumed, and that the potential fields of the atoms are spherical.

Needless to say, the results obtained for the ethyl halides do not warrant dipole moment calculations for other alkyl halides. However, it must be remembered that the primary importance of our theory is not the calculation of dipole moments, although we believe the theory does give a clear qualitative picture of "induction of bond moments" which results in such phenomena as a lower dipole moment for chloroform than for methyl chloride. The main purpose of this work is the approximate calculation of charge shifts in molecules due to substituents. In succeeding papers in this series, we shall be interested primarily in *differences* in charges on various atoms in molecules, and these are far less sensitive than dipole moments to inaccuracies in the parameters of the theory. As an illustration of this point, consider ethyl iodide, the molecule listed in Table II where the value of the methane CH moment makes the most difference in the value of the calculated moment of the molecule. Here the quantity $\epsilon_1 - \epsilon_2$ (where ϵ_1 is the charge on the carbon attached to the iodine and ϵ_2 is the charge on the other carbon) has the values 0.301, 0.298, and 0.295 (in units of 10^{-10} e.s.u.) for C^-H^+ moments of 0.3 D, 0, and -0.3 D, respectively. Similar small variations in charge *differences* will occur for the other ethyl halides as the methane CH moment is varied. This result is of great importance, for it will enable us to calculate fairly accurately the differences in charges on atoms in molecules due to the induction of some substituent, such as a halogen. These charge differences are very important in determining relative reaction rates, as Ri and Eyring[2] have shown for the nitration of substituted benzenes, and as we shall further demonstrate in future papers in this series.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

Kinetics of the Ammonium Acetate-Catalyzed Condensation of Vanillin and Nitromethane[1]

BY THOMAS I. CROWELL AND FAUSTO A. RAMIREZ

In order to study the amine catalysis of the condensation between aldehydes and nitroalkanes the rate of reaction of vanillin with nitromethane to form 3-methoxy-4-hydroxy-β-nitrostyrene has been measured in methanol solution at 25°, using 0.5 *M* ammonium acetate as catalyst. The rate is decreased both by acid and by base, the maximum being at a *p*H slightly higher than that of ammonium acetate solutions. A small induction period was observed in the otherwise first-order course of the reaction of vanillin with excess nitromethane. The disappearance of this induction period when vanillin is allowed to react with ammonium acetate, before adding nitromethane, indicates an intermediate tentatively formulated as the imine. Accordingly the acetates of secondary and tertiary amines are shown to be much less effective catalysts than ammonium and *n*-butylammonium acetates. Ammonium acetate reacts with the above nitrostyrene in dry methanol, forming products which hydrolyze to vanillin.

Various substituted β-nitrostyrenes have been prepared by the action of a strong base on nitromethane and an aromatic aldehyde.[2] The mechanism[3] is probably attack on the carbonyl group by the anion of nitromethane, followed by dehydration. In some cases the intermediate nitroalcohols have been isolated; all the synthetic procedures call for a dehydrating agent in the final step.[4] The condensation also proceeds in less basic or even in acid solution when amines are used as catalysts. Useful conditions range from a trace of a primary amine, without solvent, to ammonium acetate in glacial acetic acid.[2] In order to elucidate the role of the amine, we have studied the rate of condensation of vanillin with nitromethane to form 3-methoxy-4-hydroxy-β-nitrostyrene (VNM), a highly colored acid–base indicator.[5] This particular reaction appeared clean-cut, with stable reactants and product.

The reaction was run in methanol at 25° and in most cases was catalyzed by 0.500 *M* ammonium acetate. The rate was determined by gravimetric analysis for vanillin as the 2,4-dinitrophenylhydrazone.

Experimental

Materials.—VNM was prepared according to Knoevenagel and Walter.[5a] Nitromethane and the amines used were carefully fractionated in a packed column. Alkylammonium acetates were prepared in solution by adding methanolic acetic acid to a weighed quantity of amine. The solvent was Eimer and Amend reagent methanol.

Eimer and Amend C.P. ammonium acetate was dried about two hours at 0.07 mm. pressure and thereafter handled in a dry-box. Analysis for ammonia by evaporation from standard base gave 22.13% NH_3 (Calcd. 22.09%).

Vanillidene methylamine was prepared by the method of Moffett and Hoehn.[6] The large plates obtained from benzene, m.p. 131–135°, turned yellow in solution or in moist air.

Procedure.—The regular kinetic experiments were started by adding 10 ml. of standard nitromethane solution to 1.927 g. (0.025 mole) of ammonium acetate in 25 ml. of methanol, then adding 10 ml. of standard vanillin solution at zero time and diluting to 50 ml. Samples were withdrawn with a 5-ml. pipet and added to the hot precipitating reagent. (This reagent was prepared by dissolving 1.0 g. of 2,4-dinitrophenylhydrazine in 60 ml. of concd. sulfuric acid and diluting to 1 liter with water. For analysis of a 0.027 *M* vanillin solution, 40 ml. of this solution was filtered, diluted to 140 ml. and heated to 70°.) The precipitated 2,4-dinitrophenylhydrazone was digested on the hot-plate for ten minutes, then collected in a medium-porosity sintered gooch crucible, dried two hours at 115° and weighed.[7] Five determinations on a known vanillin solution showed an average deviation from the mean of 0.4% (0.17 mg. in weight of precipitate) and an error of 0.05% from the calculated value.

Pure VNM could be obtained by diluting the reaction mixture with water and in one case was isolated in 78% yield, m.p. 166–168°. The nitrostyrene was also obtained by allowing nitromethane to react with vanillidene methylamine in dry methanol, glacial acetic acid or dioxane, then diluting with water.

Effect of *p*H.—The concentrations of acetic acid and of ammonia were varied in several runs. Acidic solutions were obtained by adding weighed portions of glacial acetic acid. The ammonia concentration was conveniently increased at constant salt concentration by adding sodium methoxide solution to the ammonium acetate solution.

The Reverse Reaction.—To a solution of 2.037 g. of ammonium acetate in dry methanol was added 0.0245 g. of VNM. The first sample produced no precipitate with hot DNP reagent, but a sample taken after five days yielded 7 mg. of vanillin 2,4-dinitrophenylhydrazone, m.p. 269–271°. VNM also formed products hydrolyzing to vanillin when treated with butylamine in methanol or ammonium acetate in acetic acid. An aqueous solution of VNM at 100°, red because of increased ionization at the high temperature, slowly produced vanillin. This hydrolysis was retarded if enough HCl was added to turn the indicator yellow.

Results

The course of a typical run is shown in Fig. 1 and on a larger scale in the lower curve of Fig. 2. The ordinate, w, is $[1/(b - a)] \ln [a(b - x)/b(a - x)]$, where a and b are the initial concentrations of vanillin and nitromethane, and $a - x$ the concentration of vanillin at time t. After a short induction period the plot is linear up to about 65% reaction. When a larger excess of nitromethane was used, the linear relation held for 90% or more of the reaction;

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