Electrostatics and the Chemical Bond. II. Unsaturated Hydrocarbons[1a]

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Abstract: An electrostatic model previously proposed for estimating heats of formation of saturated hydrocarbons has been expanded to include unsaturated hydrocarbons: alkenes, alkynes, and aromatic compounds. Formal charges of $+0.28 \times 10^{-10}$, $+0.32 \times 10^{-10}$, and $+0.36 \times 10^{-10}$ esu are assigned to H atoms bonded to saturated, double- and triple-bonded carbon atoms, respectively, with a neutralizing opposite formal charge on the attached C atom. $C-C_d$ and $C-C_t$ bonds are assigned formal charges of ± 0.12 and ± 0.16, respectively, where C_d is a vinyl or benzyl. C atom, and C_t is a triple bonded C atom. The negative end is assigned to the unsaturated carbon. Summing up all the electrostatic interactions in the hydrocarbon molecule, a unique value for the electrostatic energy (E_{el}) is obtained. This leads to a simple formula for the standard enthalpies of formation for unifunctionally unsaturated hydrocarbons given by $\Delta H_f{}^\circ{}_{298}(\text{hydrocarbon}) = \Sigma_i m_i \cdot \Delta H_f{}^\circ{}_{i,298}(\text{bonds}) + E_{el}$, where m_i is the number of bonds in the hydrocarbon of a given type and $\Delta H_f{}^\circ{}_{i,298}$ its incremental, additive contribution to $\Delta H_f{}^\circ$ at 298 K. It is also shown that the method of formal charges can give good agreement between calculated and observed dipole moments of various unsaturated hydrocarbons.

A model of the C-H bond in alkanes has been proposed,[1b] in which each H atom in an alkane molecule bears a formal charge of $+0.278 \times 10^{-10}$ esu (0.0581 electronic charge) and each C atom, a neutralizing negative formal charge. Summing up all of the electrostatic interactions in an alkane due to these formal charges gives rise to a net stabilizing electrostatic energy for each alkane, $E_{el}(C_nH_{2n+2})$, which depends only on the geometrical structure. This was then shown to lead to a surprisingly simple formula for the standard enthalpies of formation for alkanes:

$$\Delta H_f{}^\circ{}_{298}(C_nH_{2n+2},\ \text{gas}) = -2.0(n + 1) - 0.5 + E_{el}(C_nH_{2n+2})$$

This fits the observed values of $\Delta H_f{}^\circ{}_{298}$ for all the *n*-alkanes and for the branched alkanes up to C_7H_{16} to ± 0.2 kcal/mol. The maximum deviation is -0.7 kcal/mol. It was also shown that the observed dipole moments of propane and *i*-C_4H_{10} agree well with formal charge distribution if proper account is taken of mutual group polarization.

It was further suggested that the barrier to rotation about single bonds, small deviations from tetrahedral geometry, and the unfavorable gauche conformations in hydrocarbons can be quantitatively accounted for by a purely repulsive nonbonded $H \cdots H$ interaction originally proposed by Huggins.[2]

In the present paper, the model described above is expanded to include the unsaturated hydrocarbons, e.g., alkenes, alkynes, and aromatic compounds.

The Electrostatic Model of the Unsaturated Hydrocarbons Hydrocarbons

In our preceding paper,[1a] we were able to assign the single, unknown, formal charge, $\pm y$, across the C-H bond by ascribing the entire heat of isomerization of a C_4 or C_5 alkane to the change in electrostatic energy. In the case of monoolefins, the problem is more complex. Instead of a single variable, we have two: the charge separation $\pm y'$, across the C_d-H bond, and $\pm\delta'$, the charge separation across the $C-C_d$ bond. We use the notation that C_d represents one of the C atoms in a double bond, C_t the C atom in a triple bond, and C_b the C atom in a benzene ring.

It is reasonable to expect that hydrogen atoms, bonded to an sp^2 or sp C atom in unsaturated hydrocarbon compounds, will bear a different formal charge than H atoms attached to saturated C atoms. The formal charge on H atoms connected to an olefinic carbon should be higher since the carbon nucleus is less shielded by the compressed π-bond electrons than by the electrons in the two σ bonds. By the same reasoning, it is expected that a triple-bonded C atom will appear more electronegative to its ligand neighbors since its nucleus is even less shielded by the four π-bond electrons than is a double-bonded carbon nucleus. The result is that the H atom, bonded to an acetylenic carbon, will donate more of its electron cloud to the triple-bonded carbon atom and, as we shall see, will have an even larger positive formal charge. In all cases, the formal charge on the C atom is equal and opposite to its ligand charges.

That sp, sp^2, and sp^3 carbon atoms differ in their electronegativity is a reasonable conclusion from dipole-moment measurements. The observed dipole moments for bromoethane, bromoethylene, and bromoacetylene[3] are 1.80-2.00, 1.28-1.40, and 0 D, respectively. The differences in the electronegativity of various hybrid carbon atoms are responsible for an additional formal charge in the case of unsaturated hydrocarbon molecules which contain different hybridized carbon atoms. In this case, the unsaturated carbon has an additional negative charge which is neutralized by its near-neighbor carbon atom.

The formal charge distribution of various unsaturated hydrocarbons is illustrated in Figure 1. In the isobutene molecule, the methylene carbon atom will have an additional charge of $2\delta'$ to neutralize the unsaturated carbon. In the methylacetylene molecule, y and y'' are the charges due to the C-H and C_t-H bonds, and δ'' is the formal charge due to the differences in the electronegativity of C(sp^3) and C(sp^2) atoms. Note that $y \neq y' \neq y''$, and $\delta' \neq \delta''$. The charge distribution of ethylbenzene is also given in Figure 1. Charge distributions in all other unsaturated hydrocarbons will follow the same model.

In treating the unsaturated compounds, we begin by writing a general charge distribution as shown in Figure 1 for isobutene, methylacetylene, and ethylbenzene. We have assumed that, in the saturated groups (e.g., CH_2, CH_3), the formal charges across bonds remain the same as in the alkanes. For the olefins, this makes the electrostatic energy (E_{el}) a homogeneous quadratic function of the charges y (alkane C-H), y', and δ'. In eq 1, the coefficients a_{ij} are numerical factors determined completely by the geometry of the molecules, and q_iq_j are the charges on the *i*th and *j*th

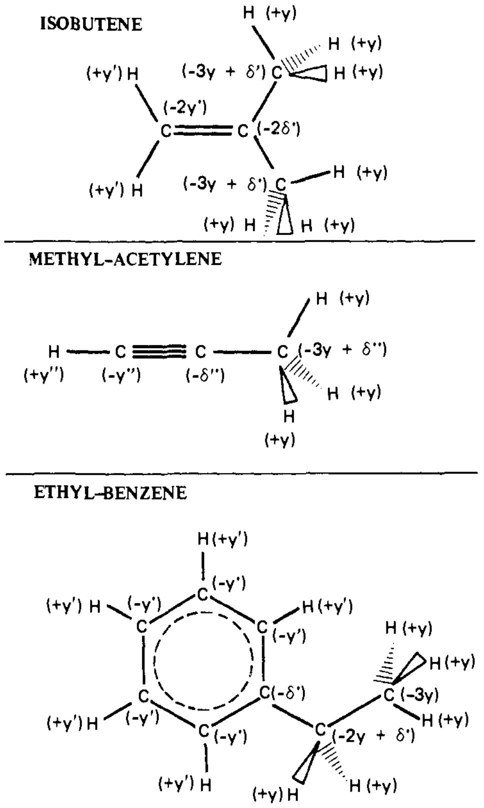

Figure 1.

$$E_{\text{el}} = \sum_{i=1}^{n} \sum_{j=i+1}^{n} q_i q_j / r_{ij} = a_{1,1}y^2 + a_{2,2}y'^2 + a_{3,3}\delta'^2 + a_{1,2}yy' + a_{1,3}y\delta' + a_{2,3}y'\delta' \quad (1)$$

atom, and $r_{i,j}$ is their distance apart. Similar equations can be obtained for acetylenes and aromatics.

So, for every given hydrocarbon molecule with a known geometry, the electrostatic energy could be written as a function of the formal charges, y, y', y'', δ', δ'', and the distances, $r_{i,j}$. For calculating the distances between nonbonded atoms, we have assumed that C(sp^2) orbitals are coplanar and C(sp) orbitals are linear.

The distances between bonded atoms and the angles between bonds which have been used for the compilation of E_{el} are summarized in Table I. E_{el} is relatively insensitive to small variations of intramolecular distances or angles. The values of bond lengths and angles given fit all the studied molecules within about ±½%; thus the attendant errors in E_{el} for the various molecules are less than ±½%.

The electrostatic model by itself is not enough to account for the heats of formation of any given hydrocarbon. There is always a relatively large contribution from nonelectrostatic stabilizing or destabilizing energies to the chemical bond. To account for the nonelectrostatic part of the chemical bond, one can use one of the simple additivity laws.[4-6] A modification of the law of bond additivity, in which somewhat different values have been assigned for the chemical bond heats of formation, seemed to us the best way to account for the nonelectrostatic part of the chemical bond. The heats of formation of any given hydrocarbon can be written as the sum of the electrostatic and the nonelectrostatic stabilizing energies and is given by:

$$\Delta H_f{}^{\circ}{}_{298} = \sum_i m_i \Delta H_f{}^{\circ}{}_{i,298}(\text{bond}) + E_{\text{el}} \quad (2)$$

where m_i is the number of bonds in the molecule which have the same character (e.g., C_t-C_t, C_d-C, C_d-H, etc.), and $\Delta H_f{}^{\circ}{}_{i,298}$ represents their additive contribution to $\Delta H_f{}^{\circ}$ of the compound.

Table I. Bond Lengths and Angles of Various Unsaturated Hydrocarbons

Bond	Distance, Å
C—C	1.543
C_b—C_b	1.396
C_d═C_d	1.339
C_t≡C_t	1.207
C_d—C	1.510
C_t—C	1.467
C—H	1.093
C_d—H	1.070
C_t—H	1.059
C_b—H	1.084
Angle	**Degrees**
C≡C—H, C≡C—C	180 (linear)
C—C_d—C	120 (coplanar)
C—C—C, C—C—H, H—C—H	109.47 (tetrahedral)
C═C—H	120 (coplanar)
C═C—C	123 (coplanar)

The Alkenes

The values of the electrostatic energy of various alkenes as functions of the formal charges are summarized in Table II. To determine the absolute values of the various formal charges, we have examined the heats of reactions in which bonds are conserved. In such reactions, it is expected that the heat of the reaction is purely a result of the differences in the electrostatic energy of the reactants and the products. In the alkene family, several reactions of this kind can be written (I-IV). Of these reactions, reaction II seemed to us

$$C_2H_4 + 2\text{-}C_4H_8(\text{trans}) \longrightarrow 2C_3H_6 - 0.4 \text{ kcal} \quad (I)$$

$$i\text{-}C_4H_8 \longrightarrow trans\text{-}2\text{-}C_4H_8 - 1.3 \text{ kcal} \quad (II)$$

$$C_2H_4 + n\text{-}C_5H_{10} \longrightarrow C_3H_6 + i\text{-}C_4H_8 - 1.7 \text{ kcal} \quad (III)$$

$$C_2H_4 + n\text{-}C_6H_{12} \longrightarrow n\text{-}C_5H_{10} + C_3H_6 - 1.2 \text{ kcal} \quad (IV)$$

the best one to determine the parameters y' and δ' since reaction I is almost thermoneutral and, as we shall show later, trimethylethene and tetramethylethene have significant nonbonded H...H repulsions. The difference in the electrostatic energies between *trans*-2-C_4H_8 and *i*-C_4H_8 can be determined from Table II and is given by eq 3. The

$$\Delta E_{\text{el}} = -0.13y^2 + 1.39y'^2 + 0.63yy' + 1.13\delta'^2 - 0.58y\delta' + 1.01y'\delta' \quad (3)$$

value of y is already known from the alkanes study;[1a] hence, by equating ΔE_{el} to the heat of reaction II, one can obtain sets of values of y' and δ' which will give an agreement with the heats of reaction II. Appendix I shows the difference in electrostatic energy between *trans*-2-C_4H_8 and *i*-C_4H_8 as a function of formal charges y' and δ'. Since a unique choice of charges y' and δ' cannot be made, we have chosen the values of $\delta' = 0.12 \times 10^{-10}$ esu and $y' = 0.32 \times 10^{-10}$ esu ($^1/_{40}$ and $^1/_{15}$ of electron charge, respectively).[13] By substituting y, y', and δ' with the above-mentioned values, E_{el} can be easily obtained and is shown on the first column of Table III.

For determining the heats of formation of the alkenes, we use reactions V-VII.[14] The heats of these reactions can be

Reaction	ΔH_r	
2C(diamond) + 2H_2(g) ⟶ C_2H_4(g)	11.4 kcal	(V)
3C(diamond) + 2H_2(g) ⟶ C_3H_4(g)	44.1 kcal	(VI)
3C(diamond) + 3H_2(g) ⟶ C_3H_6(g)	3.4 kcal	(VII)

Table II. Electrostatic Energies of the Alkenes

Alkene	Electrostatic energy (E_{el}), esu^2 Å^{-1}
Ethene	$-5.67y'^2$
Allene	$-6.21y'^2$
Propene	$-6.57y^2 - 3.82y'^2 + 0.82yy' - 0.67\delta'^2 + 3.35y\delta' - 0.76y'\delta'$
1-Butene	$-9.05y^2 - 3.84y'^2 + 0.38yy' - 0.66\delta'^2 + 1.83y\delta' - 0.78y'\delta'$
1,1-Dimethylethene	$-12.94y^2 - 3.14y'^2 - 0.34yy' - 2.24\delta'^2 + 7.47y\delta' + 0.80y'\delta'$
cis-2-Butene	$-13.02y^2 - 1.66y'^2 + 0.86yy' - 1.03\delta'^2 + 6.88y\delta' - 1.97y'\delta'$
trans-2-Butene	$-13.07y^2 - 1.75y'^2 + 0.97yy' - 1.11\delta'^2 + 6.89y\delta' - 1.81y'\delta'$
Trimethylethene	$-19.37y^2 - 0.94y'^2 + 0.58yy' - 2.41\delta'^2 + 11.24y\delta' - 0.75y'\delta'$
Tetramethylethene	$-25.59y^2 - 3.49\delta'^2 + 15.83y\delta'$

Table III. Comparison of Calculated and Observed Values of $\Delta H_f{}^\circ{}_{298}$ (kcal mol^{-1}) for Alkenes

Compd	E_{el}	$\Delta H_f{}^\circ{}_{298}{}^7$ (obsd)	$\Delta H_f{}^\circ{}_{298}$ (calcd)	Δ (calcd − obsd)	Δ'[a] (calcd − obsd)
Ethene	−8.36	12.4	12.4	0.0	0.0
Allene	−9.16	45.6	45.6	0.0	0.0
Propene	−11.01	4.9	4.9	0.0	0.0
1-Butene	−15.07	−0.2	−1.2	−1.0	−1.0
1,1-Dimethylethene	−15.21	−4.3	−4.2	+0.1	+0.4
cis-2-Butene	−14.01	−1.9	−3.0	−1.1	−0.1
trans-2-Butene	−13.98	−3.0	−2.8	+0.2	+0.2
Trimethylethene	−17.98	−10.1	−11.8	−1.7	−0.4
Tetramethylethene	−21.95	−16.4	−20.7	−4.3	−1.7

[a] Δ' is calculated by assigning 1.0 kcal to the 1–4 nonbonded cis H···H repulsion due to vicinal methyl and 0.3 kcal to the repulsion of the 1–5 H···H repulsion of the H atoms located on the geminal methyl groups in isobutene.

written in terms of the net making and breaking of bonds and changes in E_{el} (eq 4-6). Since by symmetry the elements in these reference states will not have any electrostatic stabilizing energy, we can replace ΔE_{el} in eq 4-6 by E_{el},

$$\Delta H_r{}^\circ{}_{298}(\mathrm{V}) = \Delta H_f{}^\circ{}_{298}(\mathrm{C_d{=}C_d}) + 4\Delta H_f{}^\circ{}_{298}(\mathrm{C_d{-}H}) + \Delta E_{el} - 4\Delta H_f{}^\circ{}_{298}(\mathrm{C{-}C}) - 2\Delta H_f{}^\circ{}_{298}(\mathrm{H{-}H}) \quad (4)$$

$$\Delta H_r{}^\circ{}_{298}(\mathrm{VI}) = 2\Delta H_f{}^\circ{}_{298}(\mathrm{C_d{=}C_d}) + 4\Delta H_f{}^\circ{}_{298}(\mathrm{C_d{-}H}) + \Delta E_{el} - 6\Delta H_f{}^\circ{}_{298}(\mathrm{C{-}C}) - 2\Delta H_f{}^\circ{}_{298}(\mathrm{H{-}H}) \quad (5)$$

$$\Delta H_r{}^\circ{}_{298}(\mathrm{VII}) = \Delta H_f{}^\circ{}_{298}(\mathrm{C_d{=}C_d}) + \Delta H_f{}^\circ{}_{298}(\mathrm{C_d{-}C}) + 3\Delta H_f{}^\circ{}_{298}(\mathrm{C_d{-}H}) + 3\Delta H_f{}^\circ{}_{298}(\mathrm{C{-}H}) + \Delta E_{el} - 6\Delta H_f{}^\circ{}_{298}(\mathrm{C{-}C}) - 3\Delta H_f{}^\circ{}_{298}(\mathrm{H{-}H}) \quad (6)$$

and since, by definition, the heats of formation of the elements are equal to zero, we must assign a value of zero to the heats of formation of bonds *in* the reference state. $\Delta H_f{}^\circ{}_{298}$(C-C) will be equal to 0.25 kcal (the heat of formation of diamond from graphite divided by the number of bonds per mole), and since we know from our previous work[1b] that:

$$\Delta H_f{}^\circ{}_{298}(\mathrm{C{-}C}) + \Delta H_f{}^\circ{}_{298}(\mathrm{H{-}H}) - 2\Delta H_f{}^\circ{}_{298}(\mathrm{C{-}H}) = -2.5 \text{ kcal} \quad (7)$$

we can assign the value of −1.13 kcal mol^{-1} to $\Delta H_f{}^\circ{}_{298}$(C-H). Substituting all the known parameters in eq 4-6, one can get 4A-6A. Simultaneous solution of, e.g.,

$$11.4 = \Delta H_f{}^\circ{}_{298}(\mathrm{C_d{=}C_d}) + 4\Delta H_f{}^\circ{}_{298}(\mathrm{C_d{-}H}) - 9.36 \quad (4\mathrm{A})$$

$$44.1 = 2\Delta H_f{}^\circ{}_{298}(\mathrm{C_d{=}C_d}) + 4\Delta H_f{}^\circ{}_{298}(\mathrm{C_d{-}H}) - 10.16 \quad (5\mathrm{A})$$

$$3.4 = \Delta H_f{}^\circ{}_{298}(\mathrm{C_d{=}C_d}) + 3\Delta H_f{}^\circ{}_{298}(\mathrm{C_d{-}H}) - 20.70 \quad (6\mathrm{A})$$

eq 4A-6A, gives us the three bond values. The values are: $\Delta H_f{}^\circ{}_{298}(\mathrm{C_d{-}H}) = -3.3$, $\Delta H_f{}^\circ{}_{298}(\mathrm{C_d{=}C_d}) = 34.0$, and $\Delta H_f{}^\circ{}_{298}(\mathrm{C_d{-}C}) = -5.5$ kcal mol^{-1}. Substituting the bond parameters and the electrostatic energy in eq 2, the heats of formation of the alkenes are obtained. Table III shows the comparison between the calculated and observed heats of formation for various alkenes.

To this point we have neglected the destabilizing energies associated with H ··· H nonbonded repulsions. Though the potential-energy curves of these repulsions are known,[2] accurate calculation of the energies requires precise (i.e., ±0.01 Å) geometrical information. At this stage we can only estimate the corrections that should be made. By taking into account all the repulsions in the molecule due to pairs of nonbonded H atoms, a corrected value for the heats of formation of the alkenes can be made which will give a much better agreement with the observed heats of formation.

We will not do this in the present paper. Instead we will make corrections only in the interaction of vicinal methyl (cis) and geminal methyl groups in the double bond. This improves the agreement as shown in Table III.

The Aromatics

The aromatic hydrocarbons are expected to show a similar electrostatic behavior to the alkenes since both have sp^2 hybridized C atoms. The electrostatic energies of various simple aromatic hydrocarbons as functions of the formal charges are summarized in Table IV.

To determine the values of y' and δ', one can again consider reactions in this family that conserve bonds. The only

Table IV. Electrostatic Energies of the Aromatic Hydrocarbons

Compd	Electrostatic energy (E_{el}), esu^2 Å^{-1}
Benzene	$-3.92y'^2$
Toluene	$-6.53y^2 - 3.53y'^2 - 0.66\delta'^2 + 0.26yy' + 3.33y\delta' + 0.64y'\delta'$
Ethylbenzene	$-9.04y^2 - 3.53y'^2 - 0.66\delta'^2 + 0.25yy' + 1.84y\delta' + 0.64y'\delta'$
o-Xylene	$-13.01y^2 - 2.96y'^2 - 1.06\delta'^2 + 0.35yy' + 7.92y\delta' + 0.83y'\delta'$
m-Xylene	$-13.08y^2 - 3.10y'^2 - 1.24\delta'^2 + 0.44yy' + 6.89y\delta' + 1.14y'\delta'$
p-Xylene	$-13.10y^2 - 3.11y'^2 - 1.26\delta'^2 + 0.46yy' + 6.72y\delta' + 1.17y'\delta'$

Table V. Comparison of Calculated and Observed Values of $\Delta H_{f}{}^{\circ}{}_{298}$ (kcal mol^{-1}) for Aromatics

Compd	E_{el}	$\Delta H_{f}{}^{\circ}{}_{298}$ (obsd)	$\Delta H_{f}{}^{\circ}{}_{298}$ (calcd)	Δ (obsd − calcd)
Benzene	−5.78	19.8	20.0	−0.2
Toluene	−10.46	12.0	12.1	−0.1
Ethylbenzene	−13.98	7.2	6.6	0.6
o-Xylene	−14.53	4.6	4.9	−0.3
m-Xylene	−15.07	4.1	4.3	−0.2
p-Xylene	−15.14	4.3	4.3	0.0

reaction in which bonds are conserved is the reaction of two toluene molecules to give benzene and *p*-xylene (eq VIII).

$$2CH_3{-}C_6H_5 \longrightarrow C_6H_6 + p\text{-}(CH_3)_2C_6H_4 - 0.1\ \text{kcal} \quad \text{(VIII)}$$

The differences in electrostatic energies for reaction VIII are given in eq 8. As one can see from this equation, ΔE_{el}(VIII) is completely insensitive to small variations in y' and

$$\Delta E_{el}(\text{VIII}) = 0.04y^2 + 0.03y'^2 + 0.06\delta'^2 - 0.06yy' + 0.06y\delta' - 0.11y'\delta' \quad (8)$$

δ'. The experimental uncertainty of the heat of reaction VIII is at least ±0.2 kcal, and any values of y' between 0 and 0.6×10^{-10} esu and of δ' between 0 and 0.25×10^{-10} esu will give a good agreement with the observed heat of this reaction. Since the differences between the values of y and y' are rather small (0.28 and 0.32×10^{-10} esu), and since we expect that aromatic hydrocarbons will show a similar behavior to olefinic hydrocarbons rather than to saturated hydrocarbons, we have chosen the same values of y' and δ' as for the olefinic hydrocarbons ($y' = 0.32$ and $\delta' = 0.12 \times 10^{-10}$ esu). The calculated values of E_{el} for several aromatic hydrocarbons are shown in Table V.

To determine the contributions of the bond heats of formation, we followed the same procedure as for the alkenes. Three equations for the formation of benzene, toluene, and *p*-xylene from the elements were written and solved for the $\Delta H_{f}{}^{\circ}{}_{298}(C_b{-}C_b)$, $\Delta H_{f}{}^{\circ}{}_{298}(C_b{-}H)$, and $\Delta H_{f}{}^{\circ}{}_{298}(C_b{-}C)$. We optimized the values within ±10% so as to give the smallest deviation between the calculated value of the heats of formation via eq 2. The values of $\Delta H_{f}{}^{\circ}{}_{298}$ for the aromatic bonds are: $\Delta H_{f}{}^{\circ}{}_{298}(C_b{-}C_b) = 6.5$, $\Delta H_{f}{}^{\circ}{}_{298}(C_b{-}H) = -2.2$, and $\Delta H_{f}{}^{\circ}{}_{298}(C_b{-}C) = -2.0$ kcal. The calculated and the observed values of heats of formation for various aromatics are summarized in Table V.

For this series, the agreement between the observed and calculated $\Delta H_{f}{}^{\circ}{}_{298}$ is excellent, but this agreement may be somewhat misleading since, in all of these hydrocarbons (except for C_6H_6), there are pairs of nonbonded H atoms which are less than 2.7 Å apart and, in some cases, they are as close as 2.4 Å. It is very probable that the final bond parameter and formal charges will differ slightly from the values that we have chosen when account is taken of the nonbonded repulsions.

The Alkynes

The electrostatic energies of some simple alkynes as functions of the formal charges are shown in Table VI.

By applying the same methods of considering bond causing disproportionation reactions, several sets of y'' and δ'' were obtained. The heats of these reactions are known only to within ±0.6 kcal. With the same requirements of physical reasonableness consistent with the foregoing families, we chose $y'' = 0.36$ and $\delta'' = 0.16 \times 10^{-10}$ esu. The electrostatic energies for some acetylenic compounds are summarized in Table VII. $\Delta H_{f}{}^{\circ}{}_{298}(C_t{-}C)$, $\Delta H_{f}{}^{\circ}{}_{298}(C_t{-}C)$, and $\Delta H_{f}{}^{\circ}{}_{298}(C_t{-}H)$ have been chosen as described before to give the best agreement with the observed heats of formation; the selected values are $\Delta H_{f}{}^{\circ}{}_{298}(C_t{-}C_t) = 67.7$, $\Delta H_{f}{}^{\circ}{}_{298}(C_t{-}H) = -5.25$, and $\Delta H_{f}{}^{\circ}{}_{298}(C_t{-}C) = -8.4$ kcal mol^{-1}. The comparison between the observed and calculated heats of formation of various acetylenic compounds is shown in Table VII. Calculated values agree to within experimental uncertainty with the reported values. No vicinal or geminal H. . .H repulsions exist in any of the compounds listed, except for the ethylacetylene.

Dipole Moments

As we have shown before, the C–H dipole moment, which can be obtained by using our proposed formal charge model, is an unexpectedly good agreement with the suggested dipole moment based on completely different studies.[8,9] The C–H and C–C dipole moments when unsaturated C atoms are involved can be easily calculated on the basis of our electrostatic model and they are: $\mu(C_d{-}H) = 0.34$ D, $\mu(C_t{-}H) = 0.38$ D, $\mu(C_d{-}C) = 0.18$ D, and $\mu(C_t{-}C) = 0.24$ D. Using these values, the known geometry of the molecule and, taking into account polarizability effects, the dipole moment of any given unsaturated hydrocarbon can be estimated. We have calculated, using these procedures, the dipole moment of three representative unsaturated hydrocarbons: methylacetylene, toluene, and propene.

The simplest case is methylacetylene. The vectorial summation of the bond dipoles along the molecule axis is 0.17 D. The induced contribution to the net dipole was estimated by calculating the induced dipole moment caused by any given bond dipole on all other atoms in the molecule except for the pair of atoms associated with the dipole. The induced moment was calculated by using eq 9, where μ_{bond} is

$$\mu_{\text{ind}} = (2\mu_{\text{bond}}/r^3)\alpha_A \quad (9)$$

the bond dipole moment, α_A is the polarizability of atom A, and r is the distance between the center of the dipole to any given atom in the molecule. The polarizability of acetylenic C atom was assumed to be 2.1 Å^3 (½ the value of C≡C bond) along the molecular axis and 0.4 Å^3 for H atom. Summing up all the components of the induced dipole along the C_2H_2 axis, a value of 0.43 D for the induced dipole is obtained. Together with the intrinsic dipole, a net dipole of 0.60 is calculated, in fair agreement with the observed dipole moment of 0.75 D.[3]

Similar calculations in the case of toluene show that the intrinsic dipole moment along the main molecule axis is 0.14 D, and the induced component of the dipole along this axis is 0.29 D, which gives a net dipole of 0.41 D again in reasonable agreement with the observed value of 0.36 D.[3]

More complicated is the case of propene. In this case, the net dipole is not along any molecular axis. The vectorial sum of the bond dipoles is 0.15 D, and its direction is about 60° from the double bond axis. The total of the induced components of the dipole is 0.15 D, and its direction is approximately 45° from the C=C bond axis; therefore the net calculated dipole moment of the molecule is 0.29 D, and its direction is 52.5° from the C=C axis, in good agreement with the observed values of 0.36 D and 33°.[11]

Discussion

The electrostatic model presented for bonding in the hydrocarbons gives a very simple picture for the relative stability of the saturated and nonsaturated hydrocarbons. Agreement between the experimental and the calculated enthalpies of formation is excellent as long as there are no large steric interactions. As shown by Huggins,[2] two nonbonded H atoms in a hydrocarbon molecule will significant-

Table VI. Electrostatic Energies of the Alkynes

Alkyne	Electrostatic energy (E_{el}), esu^2 Å^{-1}
Acetylene	$-1.64y''^2$
Methylacetylene	$-6.55y^2 - 0.94y''^2 + 0.09yy'' - 0.68\delta''^2 + 3.36y\delta'' + 0.28y''\delta''$
Ethylacetylene	$-9.04y^2 - 0.94y''^2 + 0.10yy'' - 0.68\delta''^2 + 1.87y\delta'' + 0.28y''\delta''$
Dimethylacetylene	$-13.06y^2 - 1.04\delta''^2 + 6.95y\delta''$

Table VII. Comparison of Calculated and Observed Values of $\Delta H_f{}^\circ{}_{298}$ (kcal mol^{-1}) for Alkynes

Alkyne	E_{el}	$\Delta H_f{}^\circ{}_{298}$ (obsd)	$\Delta H_f{}^\circ{}_{298}$ (calcd)	Δ (obsd − calcd)
Acetylene	−3.1	54.3	54.2	0.1
Methylacetylene	−6.9	44.4	44.2	0.2
Ethylacetylene	−9.4	39.5	39.7	−0.2
Dimethylacetylene	−10.6	34.7	34.3	0.4

Table VIII. C–C and C–H Bonds Heats of Formation

Bond	$\Delta H_f{}^\circ{}_{298}$ (bond) kcal mol^{-1}	Bond	$\Delta H_f{}^\circ{}_{298}$ (bond) kcal mol^{-1}	Bond	$\Delta H_f{}^\circ{}_{298}$ (bond) kcal mol^{-1}
C—H	−1.13	C═C	0.25	C—C	0.25
C_b—H	−2.2	C_b═C_b	6.5	C_b—C	−2.0
C_d—H	−3.3	C_d═C_d	34.0	C_d—C	−5.5
C_t—H	−5.2	C_t≡C_t	67.7	C_t—C	−8.0
C·—H	11.9[12]			C·—C	14.0[12]

Table IX

$\delta' \times 10^{10}$ esu	$y' \times 10^{10}$ esu 0.20	0.24	0.28	0.32	0.36	0.40
0.00	−1.2	−1.6	−2.1	−2.7	−3.4	−4.1
0.04	−0.8	−1.2	−1.6	−2.2	−2.8	−3.4
0.08	−0.5	−0.8	−1.2	−1.7	−2.2	−2.8
0.12	−0.2	−0.5	−0.8	−1.2	−1.7	−2.2
0.16	0.0	−0.2	−0.5	−0.8	−1.2	−1.7
0.20	0.3	0.0	−0.3	−0.5	−0.8	−1.3

ly repel each other if they are less than 2.7 Å apart. The energy associated with this repulsion could be as high as 1.0 kcal mol^{-1} in the case of two nonbonding H atoms at only 2.35 Å apart. Since these repulsive potentials vary exponentially with distance,[2] a detailed calculation of energy associated with the nonbonded interaction requires a very precise geometrical model of the hydrocarbon molecules. The actual structures of the hydrocarbons are slightly different from the ideally tetrahedral, planar, and linear forms, in such a way that nonbonded H atoms will be as far apart as possible. These small variations in the geometry of the molecules affect very little the electrostatic energy of a given molecule but reduce significantly the energy associated with nonbonded repulsions. Furthermore, the only case in which only a fair agreement between the calculated and the observed enthalpy of formation was observed was tetramethylethene. In this case, it is not sufficient to consider only the nonstabilizing energy associated with the 1,4-nonbonded interaction. Another contribution to the destabilizing energy comes from the significant deformation of this molecule from the expected 120° for the C-C_d-C angle and the nonplanar structure of the molecule. Correction for the energy associated with this deformation should give a better agreement in this case and in all other cases where the molecule is deformed in order to increase distances between nonbonded atoms. Later in this series we will consider these interactions in detail. At the moment, it seems plausible that a better agreement will be obtained.

The parameters we have chosen, e.g.; the formal charges and the heats of formation of the bonds, are not unique and have been selected to satisfy the experimentally observed values of the heats of formation. Theoretically for every family of unsaturated hydrocarbons, there are five parameters (two formal charges and three bond heats of formation); in fact, only one of these parameters is independent. Since our basic requirement from the electrostatic model was that the whole series of hydrocarbons will form a consistent scheme, the choice of the parameters was much more limited. After choosing values for the basic formal charge in the saturated hydrocarbons series, $|y| = 0.28 \times 10^{-10}$ esu, on the basis of the heats of isomerization of saturated hydrocarbons, it was necessary to choose a formal charge y' to explain the increase in the electronegativity between saturated and nonsaturated carbon atoms, and yet the choices were limited to reasonably small values for the formal charge associated with the two differently hybridized bonded C atoms. With the combination of this requirement and the fact that, in chemical reactions within a certain hydrocarbon family in which bonds are conserved, the heat of the reaction is a pure result of the changes in electrostatic energy, our choice of formal charges became very narrow. Several combinations of formal charges which satisfy one requirement or another have been checked. The values we have selected seemed to us the most reasonable values to satisfy our requirement and also be consistent with the observed dipole moments. Once the electrostatic energy of the various molecules has been determined, the determination of the bond parameters, e.g., bond heats of formation, was narrowed to an almost unique selection. We also varied these parameters, and the values that have been selected gave the most satisfying results within the limitation of this method which has so far neglected explicitly, nonbonded repulsions.

It is interesting to look at the sequences of the bonds of heats of formation as they are represented in Table VIII.

It is satisfying to observe that the stabilities of the bonds as reflected in their contribution to $\Delta H_f{}^\circ$ increase monotonically and about linearly with the electronegativity of the C atoms (columns 2 and 4). It is also satisfying to note that the triple bond energy of acetylene (C_t≡C_t) now comes out as almost exactly twice the double bond energy in olefins (C_d═C_d).

Appendix I

The differences in the electrostatic energies (ΔE_{el}, kcal mol^{-1}) between *trans*-2-butene and isobutene, after eq 3; for various y' and δ' formal charges is given in Table IX. The charge y is taken as 0.28×10^{-10} esu. The observed value for $\Delta(\Delta H_f{}^\circ{}_{298})$ is −1.3 ± kcal mol^{-1}.

References and Notes

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(13) This gives a good overall fit of the data and seems intuitively reasonable relative to the alkanes, aromatics, and acetylenes.
(14) The reason for selecting diamond as a reference state is reported in our previous paper.[1a] The heats of reactions V–VII are based on the values given by Cox and Pilcher[7] corrected for the diamond heat of formation (0.5 kcal for every C atom in the molecule).

Electrostatics and the Chemical Bond. III. Free Radicals

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Abstract: The electrostatic model proposed earlier by us has been applied to the alkyl free radicals methyl, ethyl, propyl, isopropyl, *tert*-butyl, *sec*-butyl, and neopentyl. A formal charge of $+0.12 \times 10^{-10}$ esu is assigned to the H atom in the $\dot{C}$–H bond and $+0.04 \times 10^{-10}$ esu to the C atom in the $\dot{C}$–C bond. Neutralizing negative charges are assigned to the saturated C atom in each case. Dipole moments of free radicals are evaluated from this model. Summing the electrostatic interactions in each free radical yields the total electrostatic energy of the radical. This leads to a very simple formula for estimating the enthalpies of formation of free radicals given by $\Delta H_f{}^\circ{}_{298}$(free radical) = $\Sigma_i m_i \Delta H_f{}^\circ{}_{i,298}$(bond) + E_{el}(free radical), where m_i is the number of bonds in the free radical of a given type and $\Delta H_f{}^\circ{}_{i,298}$ its incremental, additive contribution to $\Delta H_f{}^\circ$ at 298 K. This fits well the known values of $\Delta H_f{}^\circ{}_{298}$ for free radicals. The differences in C–H bond energies in saturated hydrocarbons are shown to arise mainly from differences in electrostatic interactions. They can be predicted to ±0.5 kcal with the proposed model which is well within the experimental uncertainties.

In previous papers,[2] an electrostatic model has been proposed for estimating the heat of formation of saturated and unsaturated hydrocarbons. Formal charges of $+0.28 \times 10^{-10}$, $+0.32 \times 10^{-10}$, and $+0.36 \times 10^{-10}$ esu were assigned to H atoms bonded to saturated (C–H), double-bonded (C_d–H) and triple-bonded (C_t–H) carbon atoms, respectively, with a neutralizing positive formal charge on the attached C atom. An additional two pairs of opposing formal charges were involved when saturated C atom is bonded to olefinic (C_d), aromatic (C_b), and acetylenic (C_t) C atoms, with the negative end in each case on the unsaturated C atom. Summing up all the electrostatic interactions in the hydrocarbon molecule then gives what we have defined as the electrostatic energy (E_{el}) of the molecule. This leads to a simple formula for the standard enthalpies of formation for saturated and unsaturated hydrocarbons, given by eq 1,

$$\Delta H_f{}^\circ{}_{298}(\text{HC}) = \sum_i m_i \Delta H_f{}^\circ{}_{i,298}(\text{bond}) + E_{el}(\text{HC}) \qquad (1)$$

where m_i is the number of bonds in the molecule of a given type i, and $\Delta H_f{}^\circ{}_{i,298}$ represents their additive contribution to $\Delta H_f{}^\circ$ of the compound. This was found to fit reasonably well the observed values of $\Delta H_f{}^\circ$ for both saturated and simple unsaturated hydrocarbons. Better agreement with the observed values was obtained by including explicitly nonbonded H · · · H repulsive interactions for H atoms not attached to the same C atom.

It was also shown[2] that the dipole moments of these same hydrocarbons can be explained on the basis of the proposed model.

In this paper, the electrostatic model is extended to free radicals.

The Electrostatic Model

Using the method of assigning formal charges to various atoms in the hydrocarbon molecule, as has been proposed previously,[2] one can write a formal charge distribution for the free radical. For the saturated part of the free radical, we use the basic formal charge of the alkanes.[2a] $+y$ is assigned to each H atom, with a neutralizing $-y$ charge to its bonded C atom. For the nonsaturated part of the radical, a formal charge of $+y_r$ is assigned to the H atom and $-y_r$ to the attached radical $\dot{C}$ atom; similarly from the $\dot{C}$–C bond, a charge of $-\delta_r$ is assigned to the C atom and $+\delta_r$ to the $\dot{C}$ atom. The charge distribution of ethyl radical is shown in Figure 1.

The electrostatic stabilizing energy is the sum of the interactions of all the formal charges presented in the radical and is given by

$$E_{el} = \sum_{i=1}^{n} \sum_{j=i+1}^{n} q_i q_j / r_{i,j} \qquad (2)$$

where $r_{i,j}$ is the distance between atoms i and j bearing charges q_i and q_j, and n is the number of atoms in the molecule. The geometry of the free radical is not known as well as the geometry of the hydrocarbons, but it is reasonable to assume that the angles and distances are similar to those obtained for alkanes and alkenes. We assume that the $\dot{C}$ radical center has properties similar to the sp^2 C atoms in olefins and aromatics. The values of bond lengths and angles which were used for this study are listed in Table I.

In justification for such a simplification, it should be mentioned here that E_{el} is insensitive to small variations in the intramolecular distances. Intramolecular distances different by 1–2% from the values listed in Table I change E_{el} by less than 1%.