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(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,

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

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

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

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%.

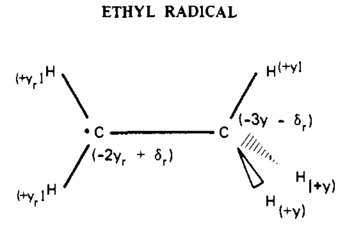

Figure 1. Illustration of the formal charge distribution of ethyl radicals.

Table I. Bond Length and Angle Estimations for Free Radicals

Bond	Distance, A
C˙—H	1.07
C˙—C	1.51
C—C	1.54
C—H	1.09
Angle	Degrees
C—C˙—C, C—C˙—H, H—C˙—H	120 (coplanar)
C—C—C, C—C—H, H—C—H	109.47 (tetrahedral)

With the definition of the formal charge distribution and the knowledge of the intramolecular distances, algebraic expressions for the electrostatic energies of the free radicals can be written. The values for seven common free radicals are listed in Table II.

Estimating the Heats of Formation of Free Radicals

As noted earlier,[2] the electrostatic model by itself is not enough to account for the total $\Delta H_f°_{298}$ of the molecules. Accounting for the nonelectrostatic part of the chemical bond is done by using additivity laws, in particular the law of bond additivity,[3] but with slightly different bond parameters than those originally proposed.[4]

The electrostatic model, as we have employed it, is a method for accounting for 1, 3, and higher, nonbonded interactions based on ionic interactions. It decomposes the total heat of formation of a molecule, ion, or radical into additive bond contributions, bonded and nonbonded electrostatic interactions, small nonbonded electrostatic interactions, and small nonbonded van der Waals interactions for atoms which are not bonded to a common atom (1, 4, or higher) algebraically (eq 3).

$$\Delta H_f°(\text{molecule}) = \sum_i m_i \Delta H_f°_{i,298} + \sum_{i=1}^{n} \sum_{j=i+1}^{n} q_i q_j / r_{i,j} + \sum_{i=1}^{n} \sum_{j=i+2}^{n} V_{i,j} \ldots \quad (3)$$

The last van der Waals term is in general small except for highly branched molecules and, except for cis and ortho effects, we have chosen so far not to consider it explicitly. Thus eq 3 reduces to eq 1.

Estimation of the heat of formation of free radicals requires the knowledge of four parameters, y_r, δ_r, $\Delta H_f°_{298}(\text{C}^\cdot\text{-C})$, and $\Delta H_f°_{298}(\text{C}^\cdot\text{-H})$, in addition to the known parameters[2] ($|y| = 0.28 \times 10^{-10}$ esu; $\Delta H_f°_{298}(\text{C-H}) = -1.13$ kcal mol^{-1}; and $\Delta H_f°_{298}(\text{C-C}) = 0.24$ kcal mol^{-1}). In principle, the best way to determine the formal charges is from consideration of the heat of a reaction in which bonds are conserved, such as eq 4. Based on eq 1, for

$$C_2H_5\cdot + C_3H_8 \longrightarrow C_3H_7\cdot + C_2H_6 + 0.3 \text{ kcal} \quad (4)$$

such bond conserving reactions (isodesmic) (Pople, etc.), ΔH_r is just equal to the differences between the electrostatic energies of reactants and products.

However, the heat of this reaction is known only to ±1.5 kcal, and it turns out that many reasonable choices of charges will satisfy this requirement. A more sensitive way for determining the new parameters was selected by taking the heat of formation of methyl and *tert*-butyl radicals as starting points. The heats of formation of these two radicals are each functions of only two out of the four new parameters and are mutually independent. On applying eq 1 to methyl and *tert*-butyl free radicals, eq 5 and 6 result. It can

Table II. Electrostatic Energy of the Free Radicals

Radical	Electrostatic energy (E_{el}), esu^2 Å^{-1}
Methyl	$-6.79y_r^2$
Ethyl	$-6.55y^2 - 3.20y_r^2 + 0.68yy_r - 0.66\delta_r^2 - 3.33y\delta_r + 2.30y_r\delta_r$
Propyl	$-9.04y^2 - 3.20y_r^2 + 0.61yy_r - 0.66\delta_r^2 - 1.84y\delta_r + 2.30y_r\delta_r$
Isopropyl	$-12.92y^2 - 0.94y_r^2 + 0.68yy_r - 0.57\delta_r^2 - 3.74y\delta_r + 0.69y_r\delta_r$
2-Butyl	$-15.47y^2 - 0.94y_r^2 + 0.59yy_r - 0.57\delta_r^2 - 3.01y\delta_r + 1.15y_r\delta_r$
tert-Butyl	$-19.10y^2 - 0.54\delta_r^2 - 4.17y\delta_r$
Neopentyl	$--16.35y^2 - 3.20y_r^2 + 2.18yy_r - 0.66\delta_r^2 + 1.15y\delta_r + 2.30y_r\delta_r$

$$\Delta H_f°_{298}(CH_3\cdot) = 3\Delta H_f°_{298}(\text{C}\cdot\text{-H}) + E_{el}(CH_3\cdot) \quad (5)$$

$$\Delta H_f°_{298}(t\text{-}C_4H_9\cdot) = 9\Delta H_f°_{298}(\text{C-H}) + 3\Delta H_f°(\text{C}\cdot\text{-C}) + E_{el}(t\text{-}C_4H_9\cdot) \quad (6)$$

be seen that $\Delta H_f°_{298}(CH_3^\cdot)$ is a function of y_r, $\Delta H_f°_{298}(t\text{-}C_4H_9^\cdot)$ is a function of δ_r, and $\Delta H_f°_{298}(\text{C-H})$ is already known. The heats of formation of all the other radicals are functions of all the four new parameters. Hence the method used in this study to determine the best parameters was to choose pairs of formal charges y_r and δ_r and to calculate the electrostatic energies of the methyl and *tert*-butyl radical. By using eq 5 and 6 and the observed heats of formation, the bond parameters $\Delta H_f°_{298}(\text{C}^\cdot\text{-H})$ and $\Delta H_f°_{298}(\text{C}^\cdot\text{-C})$ were obtained.

This type of calculation has been done for $0 < |y_r| < 0.24 \times 10^{-10}$ esu and $0 < |\delta_r| < 0.1 \times 10^{-10}$ esu. The ranges for y_r and δ_r were determined by assuming that C˙ atoms are lower in electronegativity than single bonded C atoms because of their lower ionization potentials. Since the formal charge associated with the C-H bond was determined before as $|y| = 0.28 \times 10^{-10}$ esu, this required that $|y_r| < |y|$, and that δ_r should be a smaller charge with the positive end on the C˙ atom.

For every pair of y_r and δ_r which also determined $\Delta H_f°_{298}(\text{C}^\cdot\text{-C})$ and $\Delta H_f°_{298}(\text{C}^\cdot\text{-H})$, the heats of formation of the other free radicals were calculated with the aid of eq 1. After analyzing the results and checking for the minimal deviation from the observed values of the heats of formation, we selected $|y_r| = 0.12 \times 10^{-10}$ esu and $|\delta_r| = 0.04 \times 10^{-10}$ esu as the best choices.[8] This set of y_r and δ_r fixes the (C˙-C) and the (C˙-H) heats of formation at 14.0 and 11.9 kcal mol^{-1}, respectively. The calculated heats of formation of the free radicals and the thermochemically observed values are summarized in Table III. The agreement between them is excellent and well within experimental uncertainty. One might expect that the calculated values should be lower than the observed and should be corrected for nonbonded repulsions (eq 3) but, in this case as with the alkanes,[1] the nonbonded repulsions are small. More precise calculations, which require a knowledge of distances in the molecule to within 0.01 Å, we suspect, may show that, after accounting for the nonbonded repulsions, the basic formal charge y should be slightly larger (0.29×10^{-10} esu).

Table III. Comparison of Calculated and Observed $\Delta H_f{}^\circ{}_{298}$(radical)[a]

Radical	E_{el}	$\Delta H_f{}^\circ{}_{298}$ calcd	$\Delta H_f{}^\circ{}_{298}$ obsd	Δ (obsd − calcd)
Methyl	−1.41	34.3	34.1 ± 0.5	−0.2
Ethyl	−8.12	26.3	26.4 ± 1.0	+0.1
n-Propyl	−10.73	21.6	21.5 ± 1.0	−0.1
Isopropyl	−15.55	17.6	18.2 ± 1.0	+0.6
sec-Butyl	−18.24	12.9	13.0 ± 1.0	+0.1
tert-Butyl	−23.68	8.1	8.0 ± 1.5	−0.1
Neopentyl	−21.56	7.0	7.5 ± 1.5	0.0

[a] Assuming $|y| = 0.28 \times 10^{-10}$ esu, $|y_r| = 0.12 \times 10^{-10}$ esu, and $|\delta_r| = 0.04 \times 10^{-10}$ esu; the values are in kcal mol^{-1}.

Table IV. Comparison between Electrostatic Energy of the Free Radical and Parent Molecule (E_{el} in kcal mol^{-1})

Radical	Parent molecule	E_{el} (molecule)	E_{el} (radical)	ΔE_{el} (molecule − radical)
Methyl	Methane	−12.55	−1.41	−11.14
Ethyl	Ethane	−13.57	−8.12	−5.45
n-Propyl	Propane	−16.44	−10.73	−5.71
Isopropyl	Propane	−16.44	−15.55	−0.89
sec-Butyl	*n*-Butane	−19.36	−18.24	−1.12
tert-Butyl	Isobutane	−21.17	−23.68	+2.51
Neopentyl	Neopentane	−27.73	−21.56	−6.17

Table V. Comparison of Calculated and Observed Values of C–H Bond Strength (in kcal mol^{-1})

Bond	DH°$_{298}$(R–H) calcd	DH°$_{298}$(R–H)[a] obsd	Δ (obsd − calcd)
$H-CH_3$	104.2	104 (5)	−0.2
$H-C_2H_5$	98.5	98 (5)	−0.5
H-*n*-C_3H_7	98.4	98 (5)	−0.4
H-*i*-C_3H_7	94.4	95 (5)	+0.6
H-*sec*-C_4H_9	95.0	95 (5)	0.0
H-*t*-C_4H_9	92.2	92 (5)	−0.2
H-*neo*-C_5H_{11}	99.3	100 (6)	−0.7

[a] The experimental uncertainties vary between ±0.5 and ±1.5 kcal/mol.

C–H Bond Strengths

One of the well-known and unexplained phenomena in alkanes is the differences in the C–H bond strengths which vary by more than 10% (or about 12 kcal mol^{-1}) in various alkanes. The electrostatic model gives an explanation for this phenomenon. The differences between the electrostatic energies of the parent molecule which its free radical obtained by breaking a C–H bond are summarized in Table IV.

For CH_4, the reduction is very high, ~11 kcal mol^{-1} and, for a primary H atom, the reduction is about ~5.5-6.0 kcal mol^{-1} while, for a secondary H atom, the reduction is about 1 kcal mol^{-1}. In the case of a tertiary H atom, the electrostatic stabilizing energy of the radical is by contrast higher by ~2.5 kcal mol^{-1} relative to parent alkane. This fact, and a previous suggestion that the $C^\cdot$–H and $C^\cdot$–C bonds are slightly less stable than the C–C and C–H bonds, provides a very simple explanation for the variations in the C–H bond strength. A comparison between the experimentally observed C–H bond strength and the calculated values is shown in Table V. The calculated values are based on our previously calculated heats of formation of the alkanes[1] and on the known value for the heats of formation of H atom (52 kcal mol^{-1}).[4]

Dipole Moments

If we consider each bond dipole as a fixed vector in the molecule, we should be able to make the vector sum and obtain the total dipole moment. For the alkanes whose moments are small (~0.1 D), we obtain a zero value in good agreement. Considering each $>CH_n$ group in the molecule as a group dipole with known polarizability, we could calculate induced dipoles produced by all the other groups in the molecule. This yielded very good results (to ±0.05 D) for the alkanes[2a] but only fair agreement for the unsaturated hydrocarbons[2b] whose dipole moments range from 0.360 (propylene) to 0.76 D for methylacetylene. In the case of the radicals, there are no measurements, but the present model predicts a relatively large basic dipole enhanced by a comparable induced dipole. For C_2H_5 radical, vector summation gives a moment along the $\dot{C}$–C axis of 0.12 D and an induced moment[9] of 0.34 D, giving a net moment of 0.46 D. For isopropyl radical, the basic moment is along the symmetry axis (0.14 D), the induced moment is 0.14 D, and the net is 0.28 D.

Discussion

The simple electrostatic model for nonbonded interactions has provided reasonable and quantitative explanation for some known properties of hydrocarbons. The heats of formation of most common hydrocarbons could be predicted to better than ±1 kcal mol^{-1}, the stability of branched hydrocarbons over nonbranched was explained, the spectroscopic prediction of the C–H dipole moment was shown to fit the energy-calculated value and, in some cases, the cal-

Table VI

		Formal charges × 10^{-10} esu								
	y_r	0.24	0.24	0.24	0.12	0.12	0.12	0.00	0.00	0.00
Radical	δ_r	0.00	0.03	0.06	0.00	0.03	0.06	0.00	0.03	0.06
Methyl E_{el}		−5.6	−5.6	−5.6	−1.4	−1.4	−1.4	0.0	0.0	0.0
$\Delta H_f{}^\circ(C^\cdot-H)$		13.2	13.2	13.2	11.8	11.8	11.8	11.4	11.4	11.4
tert-Butyl E_{el}		−21.6	−23.1	−24.8	−21.6	−23.1	−24.8	−21.6	−23.1	−24.8
$\Delta H_f{}^\circ(C^\cdot-C)$		13.3	13.8	14.3	13.3	13.8	14.3	13.3	13.8	14.3
Ethyl E_{el}		−9.4	−9.6	−9.8	−7.7	−8.0	−8.3	−7.4	−7.8	−8.2
$\Delta H_f{}^\circ$		26.9	27.2	27.5	25.8	26.0	26.2	25.3	25.4	25.5
n-Propyl E_{el}		−12.3	−12.3	−12.3	−10.6	−10.7	−10.8	−10.2	−10.4	−10.7
$\Delta H_f{}^\circ$		22.0	22.5	23.0	20.9	21.3	21.7	20.5	20.8	21.0
Isopropyl E_{el}		−14.7	−15.4	−16.2	−14.5	−15.3	−16.1	−14.6	−15.5	−16.5
$\Delta H_f{}^\circ$		18.3	18.6	18.8	17.1	17.3	17.5	16.6	16.7	16.7
sec-Butyl E_{el}		−17.7	−18.2	−18.8	−17.4	−18.0	−18.7	−17.5	−18.2	−19.0
$\Delta H_f{}^\circ$		13.3	13.8	14.2	12.2	12.6	12.9	11.7	12.0	12.2
Neopentyl E_{el}		−23.6	−23.3	−22.9	−21.9	−21.6	−21.4	−21.5	−21.3	−21.2
$\Delta H_f{}^\circ$		6.7	7.5	8.4	5.6	6.4	7.1	5.2	5.9	6.5

culated dipole moments of hydrocarbons can be predicted in from fair to good agreement with observations. From the work presented here, we see that variations in the C–H bond strength of hydrocarbons can also be explained in terms of pure electrostatic effects. It has also been possible to demonstrate[2a] that the barrier to rotation in ethane barrier and the instability of the gauche conformation relative to trans conformation in *n*-butane could not be explained by electrostatic interactions. These phenomena require other explanations, and the simplest is a nonbonded H · · · H repulsion of the form originally proposed by Huggins.[7] According to Huggins, a pair of H atoms attached to two different C atoms will repel each other if the distance between them is smaller than 2.7 Å. The energy associated with this repulsion can be as high as 1.0 kcal mol^{-1} for every interaction at a distance of ~2.3 Å. Once this repulsive potential is added to the electrostatic potential, an excellent agreement is obtained between the model and the experimental value for the barrier to rotation along C–C axis and for the relative instability of the gauche conformation. In some hydrocarbon molecules, the electrostatic model had predicted a heat of formation more negative than the experimental value. In all these cases, we found that at least one pair of nonbonded H atoms is separated by less than 2.5 Å. Adding the repulsion energy associated with this interaction, a better agreement with the experimental observation is obtained.

The various formal charges that we have selected in this series to explain the electrostatic stability of hydrocarbons are only an approximation, but they were consistent in all cases within the experimental uncertainty. The actual formal charges can be slightly different. This could be determined only when one will make the exact geometrical model and will take into account the exact energetic values for the H · · · H nonbonded interaction, the electrostatic interactions, and the potential function for the structure.

A preliminary calculation of $\Delta H_f°$ for compounds containing heteroatoms has already shown that this simple model by itself will not give as good an agreement with the observed results. Once an atom with a lone pair of electrons is introduced into the molecule, it appears that it is necessary to take into account the interaction between the dipole moment associated with the lone pair and the other formal charges in the molecule. Polarization effects also became significant energetically and, at the moment, we have not sorted them out.

Appendix I

The heats of formation of various free radicals, in kcal mol^{-1}, as a function of the formal charges y_r and δ_r ($|y| = 0.28 \times 10^{-10}$ esu) are given in Table VI.

References and Notes

(1) Postdoctoral Research Associate.

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(8) Calculated heats of formation of the free radicals based on the different selections of formal charges are summarized in Appendix I.

(9) Assuming polarizabilities of 1 and 2 Å^3 for C and Ċ, respectively.

Free-Radical Intermediates Produced from the One-Electron Reduction of Purine, Adenine, and Guanine Derivatives in Water

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Abstract: The one-electron reduction of purine (PH), 9-methylpurine (MP), adenosine (A) and 1-methylguanosine (MG) in water was studied using the fast-reaction technique of pulse radiolysis and kinetic absorption spectrophotometry. The hydrated electron, e_{aq}^-, and the acetone ketyl radical, $(CH_3)_2\dot{C}OH$, were used as the reducing agents. The reaction rate constants of the purine derivatives with e_{aq}^- and the $(CH_3)_2\dot{C}OH$ radical were determined at different pH values, consistent with the pK_a values of these compounds. The rate constants with e_{aq}^- were close to the diffusion-controlled limit, $k \leq 2.0 \times 10^{10}$ M^{-1} sec^{-1}. The electron transfer reaction from $(CH_3)_2\dot{C}OH$ was found to be strongly dependent on the acid-base properties of the purines and on the nature of the substituents. A correlation between the reaction rate constants with $(CH_3)_2\dot{C}OH$ and the redox potential of the purines is suggested. The transient optical absorption spectra of the free-radical intermediates produced from the reduction of the purine derivatives were determined over the pH range 0–14. The extinction coefficients and decay kinetics are also presented. These radicals undergo acid-base dissociation reactions. The pK_a values for the purine radicals $PH_4\cdot^{2+}$, $PH_3\cdot^{+}$, $PH_2\cdot$, and $PH\cdot^{-}$ are 3.2 ± 0.1, 8.5 ± 0.2, 9.9 ± 0.2, and 12.5 ± 0.2, respectively. For 9-methylpurine, the $MPH_3\cdot^{2+}$, $MPH_2\cdot^{+}$, and $MPH\cdot$ radicals have pK_a values of 2.9 ± 0.2, 6.3 ± 0.1, and 13.1 ± 0.2, respectively. For adenosine, the $AH_3\cdot^{2+}$ and $AH_2\cdot^{+}$ radicals have pK_a values of 4.6 ± 0.1 and 10.5 ± 0.1, respectively, while the ionization of $AH\cdot$ is not observed up to pH 13.6. For 1-methylguanosine, two pK_a (radical) values of ~7.0 and ≥13.0 are observed. These and other results are discussed, and tentative assignments are suggested for the various radical intermediates.

A great number of biochemical processes occur through a mechanism involving an electron transfer from a donor molecule to an acceptor molecule. The study of the one-electron reduction of the constituent bases of nucleic acids has received relatively little attention. The electrochemical reduction of pyrimidine and purine bases in aqueous and nonaqueous solutions has received the most attention, particularly through the investigations of Elving and coworkers.[2-6]