Are Radical Cation States Delocalized over GG and GGG Hole Traps in DNA?

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Recently, Kurnikov et al. (*J. Phys. Chem. B* **2002**, *106*, 7) have shown that solvation of DNA duplexes destabilizes holes of sizes larger than three base pairs. In this paper, we consider the effects of solvation and internal reorganization on the hole charge distribution in sequences 5′-X-GG-Y-3′. Radical cation states in DNA are found to be localized to a single guanine site independent of the nature of adjacent base pairs.

Introduction

Guanine (G) is known to be the most easily oxidized nucleobase, and therefore, the cation radical G^+ is a key intermediate formed by the one-electron oxidation of DNA. Created initially adjacent to an oxidant, it hops through the duplex DNA until it reacts irreversibly with molecular oxygen or water. Thus, G^+ can be generated in DNA far away from an oxidant because of hole transfer.[1−6] Fundamental mechanisms of charge migration in DNA have been discussed in terms of long-range hole hopping.[7−12] Theoretical aspects of charge transfer in DNA have recently been considered in an excellent review.[13]

In many measurements, GG doublets and GGG triplets were found to act as the most effective traps in hole transfer through DNA(see, for instance, refs 1, 5, 6, and references therein). Saito et al.[14] and Barton et al.[15] were the first who demonstrated that the long-range oxidative damage of DNA occurs specifically at the 5′-G in the 5′-GG-3′ doublets. Cleavage intensities in GGG triplets decrease in the order middle G > 5′-G > 3′-G [5,6,16,17] The map of the one-electron oxidation of DNA was studied in detail by Saito et al.[16,17] However, a low level of cleavage selectivity in GG and GGG stacks has also been experimentally demonstrated.[18]

Since electron holes are trapped at sites of minimum oxidation potentials, calculations of ionization energies of base pair sequences are useful for predicting the reactivity of different sites in DNA toward one-electron oxidation. In particular, the energy for hole transfer between two bases B and B′ can be estimated as the difference of ionization energies of these bases embedded in the duplex. Saito and co-workers reported ionization potentials (IP) for XGY triplets calculated at the HF/6-31G* level.[16,17] They concluded that the oxidation potential of G is strongly influenced by adjacent 3′- and 5′-base pairs. Quantum chemical calculations of all possible triplets 5′-XBY-3′ demonstrated that the oxidation potential of B in 5′-XBY-3′ is considerably affected by the nature of 3′-Y and becomes smaller in the order C ≈ T > A > G while the effect of the *preceding* base 5′-X is rather small.[19] The results[16,17,19] suggest that the 5′-G in GG and both Gs on the 5′-side in GGG have the lowest oxidation potentials in line with experimental findings.

A knowledge of the positive charge distribution in 5′-GG-3′ and 5′-GGG-3′ stacks is essential for interpreting experimental data and understanding details of charge transfer in DNA. On the basis of DNA photooxidation experiments, it appears to be difficult to conclude whether a hole is delocalized over adjacent guanine bases or the states where the hole is confined to different G sites are in equilibrium. Several theoretical studies have been performed to explore charge delocalization in DNA. Conwell and Basko found that the wave functions of holes trapped on Gs are extended over six base pairs.[20] Recent density functional theory (DFT) calculations performed without accounting for solvation effects suggested that a positive charge is delocalized over neighboring guanine bases.[21] Because the interaction of a charge with the polar environment considerably increases with its localization, the states with a hole confined to single bases will be favored as compared with the states where the charge is delocalized over several Gs. Beratan and his co-worker showed that the solvation effects are very important for a proper description of charge distribution in DNA models.[22] They considered in detail the interplay of two counteracting effects that determine the charge distribution in DNA. Whereas delocalization of the charge reduces the intrinsic energy of the system, the interaction with a polar environment stabilizes states with a localized hole.[22] In addition to the solvation forces, the internal (structural) reorganization energy stabilizes hole states that are spatially well-localized.[23]

In this paper, we consider the distribution of the hole charge in GG and GGG stacks using a quite simple but physically reliable model that takes into account all relevant interactions: the effect of flanking base pairs on the oxidation potential of guanine bases, the electronic coupling of GC pairs, the internal reorganization term, and the solvation of the hole states.

Model

Let us consider a system consisting of two fragments 1 and 2. In diabatic states φ_1 and φ_2, the positive charge is localized on sites 1 and 2, respectively. φ_1 and φ_2 are assumed to be orthonormalized. The state energies ϵ_1 and ϵ_2 correspond to oxidation potentials of these sites. The electronic coupling V_{12} is a measure of the electronic interaction of φ_1 and φ_2, which leads to two adiabatic states ψ_1 and ψ_2. In the ground state, $\psi_1 = c_1\varphi_1 + c_2\varphi_2$, the charges on the fragments can be defined as $q_1 = \{c\}_1^2$ and $q_2 = c_2^2 = 1 - c_1^2$. The difference $\Delta q = q_2 - q_1$ will be used to characterize the charge distribution in the system. When the charge is localized on one of two fragments,

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$|\Delta q| = 1$, and $\Delta q = 0$ when the charge is uniformly delocalized, $q_1 = q_2 = {}^1/_2$.

The charge distribution is determined by the electronic coupling V_{12} and by the difference of oxidation potentials $\Delta\epsilon = \epsilon_2 - \epsilon_1$

$$\Delta q = \frac{\Delta\epsilon}{\sqrt{\Delta\epsilon^2 + 4V_{12}{}^2}} \quad (1)$$

In turn, $\Delta\epsilon$ depends on the charge distribution. As noted in the Introduction, two terms, the internal reorganization energy r and the interaction with environment s, modulate the oxidation potentials. $\Delta\epsilon$ can be expressed by

$$\Delta\epsilon = \Delta\epsilon^0 + \Delta r + \Delta s \quad (2)$$

where $\Delta\epsilon^0$ is the difference in vertical ionization energies, Δr is the difference in reorganization energies of the sites, $\Delta r = r_2 - r_1$, and Δs is the difference in solvent contributions to the oxidation potential, $\Delta s = s_2 - s_1$.

For an isolated molecule j, the internal reorganization energy r_j^0 is defined as a difference of the adiabatic and vertical ionization potentials, $r_j^0 = I_j^{ad} - I_j^{vert}$, by definition $r_j^0 < 0$. It depends on the molecular structure. Olofsson and Larsson showed that the reorganization term of a moiety within a complex system can be estimated as $(I_j^{ad} - I_j^{vert})q^2$ where q is a charge on the moiety.[23] If subsystems 1 and 2 are identical, then $r_1^0 = r_2^0 = \rho$ and

$$\Delta r = (r_2 - r_1) = \rho(q_2{}^2 - q_1{}^2) = \rho\Delta q \quad (3)$$

Let us consider now how to estimate the solvation term Δs for a system containing (among other moieties) two identical sites 1 and 2 carrying charges q_1 and q_2, respectively. A state with the delocalized hole charge, $q_1 = q_2 = {}^1/_2$, will be used as the reference. Solvation contributions s_1 and s_2 to the oxidation potentials can be approximately defined as

$$s_1 \approx s_0 + \zeta\left(q_1 - \frac{1}{2}\right)$$

$$s_2 \approx s_0 + \zeta\left(q_2 - \frac{1}{2}\right)$$

Then $\Delta s = s_2 - s_1 = \zeta(q_2 - q_1) = \zeta\Delta q$. The parameter ζ can be estimated as follows. The solvation energy of the system ΔE^{solv} depends of on a charge distribution $\Delta E^{solv}(q_1,q_2) = q_1 s_1 + q_2 s_2$. For the reference state, $\Delta E^{solv}({}^1/_2, {}^1/_2) = s_0$. When the charge is localized on either of two sites

$$\Delta E^{solv}(1,0) = \Delta E^{solv}(0,1) = s_0 + \frac{1}{2}\zeta$$

And, therefore

$$\frac{1}{2}\zeta = \Delta E^{solv}(1,0) - \Delta E^{solv}\left(\frac{1}{2},\frac{1}{2}\right) \quad (4)$$

The solvation energies $\Delta E^{solv}(1,0)$ and $\Delta E^{solv}({}^1/_2,{}^1/_2)$ can be estimated using computational modeling of DNA oligomers (see below).

Thus, eq 1 may be written as

$$\Delta q = \frac{\Delta\epsilon^0 + (\rho + \zeta)\Delta q}{\sqrt{(\Delta\epsilon^0 + (\rho + \zeta)\Delta q)^2 + 4V_{12}{}^2}} \quad (5)$$

and Δq can be found by solving eq 5.

TABLE 1: Difference in the Oxidation Potentials of G_2 and G_1 in 5′-X-G_1G_2-Y-3′ Derived from the Calculated Results[19] (in eV)

Y	G	A	T	C
G-G_1G_2-Y	0.000	0.132	0.265	0.303
A-G_1G_2-Y	−0.001	0.131	0.264	0.302
T-G_1G_2-Y	−0.026	0.106	0.239	0.267
C-G_1G_2-Y	−0.036	0.096	0.229	0.277

TABLE 2: Electronic Coupling Matrix Element V_{12} (in eV) in Different Conformations of $(GC)_2$ Calculated by the Fragment Charge Method

conformation	$\lvert V_{12}\rvert$	conformation	$\lvert V_{12}\rvert$
reference[a]	**0.081**		
rise 2.88Å	0.200	rise 3.88 Å	0.029
roll 5°	0.048	roll −5°	0.126
shift 0.5 Å	0.020	shift −0.5 Å	0.136
slide 1 Å	0.004	slide −1 Å	0.056
tilt 2°	0.070	tilt −2°	0.094
twist 31°	0.034	twist 41°	0.104
average[b]	**0.077**		

[a] In the reference conformation, rise= 3.38 Å, twist =36°, and the other base-step parameters are zero. [b] Averaged over the 13 conformations of $(GC)_2$ presented in the table.

Before applying this model to DNA π-stacks, we have to estimate four parameters: the difference of vertical oxidation potentials $\Delta\epsilon^0$, the electronic coupling V_{12}, and the quantities ρ and ζ that represent internal reorganization and environmental interactions, respectively.

Parameter $\Delta\epsilon^0$. The difference of vertical oxidation potentials of G_2 and G_1 in a sequence 5′-X-G_1G_2-Y-3′ can be estimated as a difference of calculated ionization energies of the middle G in triplets 5′-GGY-3′ and 5′-XGG-3′. Table 1 compiles $\Delta\epsilon^0$ values derived from semiempirical calculations.[19] The predicted differences in oxidation potentials are in good agreement with experimental data Lewis et al.[24] Also $\Delta\epsilon^0$ values for 5′-X-G_1G_2-A-3′ and 5′-X-G_1G_2-G-3′ sequences (X = A, T, and C) agree well with values derived from DFT data.[21] However, for 5′-X-G_1G_2-Y-3′ (Y = T and C) semiempirical values are smaller by 0.1 eV than the corresponding DFT estimations and appear to be in better agreement with experiment.[25]

Electronic Couplings V_{12}. Quantum mechanical calculations of electronic couplings in DNA have been recently considered in detail.[26] The electronic coupling between base pairs is very sensitive to conformational changes of DNA.[27,28] In Table 2, we present the matrix element V_{12} between two guanines in $(GC)_2$ calculated by the charge difference method.[29] Our calculations of the electronic couplings using the GMH method of Cave and Newton[30] give very similar results. In the dimer of ideal structure (reference conformation), V_{12} is found to be about 0.08 eV (Table 2). When the twist is about 30°, the matrix element is close to zero. An average value of the coupling is calculated to be of 0.077 eV (Table 2). Thus $V_{12} = 0.08$ eV is a quite reasonable estimation.

Internal Reorganization Term Δr. The parameter $\rho = (I_j^{ad} - I_j^{vert})$ calculated for a GC Watson−Crick pair at the B3LYP/6-31G* level is −0.36 eV. This estimation is in good agreement with a value of −0.37 eV from DFT calculations of guanine.[23] The difference of experimental adiabatic[31] and vertical[32] ionization energies of guanine is −0.47 eV.

Solvation Parameter ζ. In line with eq 4, this parameter can be derived from solvation energies of oligomers calculated for states with the localized and delocalized hole charges. Kurnikov et al. found the solvent contribution to the oxidation

TABLE 3: Solvation Terms Calculated for DNA Oligomers with a Hole Localized on a Single G, ΔE_1^{solv}, and with a Hole Delocalized over Two Gs, ΔE_2^{solv} (in eV) [22]

	model 1[a]	model 2[a]	model 3[a]
ΔE_1^{solv}	−1.857	−1.927	−1.390
ΔE_2^{solv}	−1.451	−1.536	−0.913
$\zeta = 2(\Delta E_1^{solv} - \Delta E_2^{solv})$	−0.812	−0.782	−0.954

[a] Uniform charge distribution was assumed in models 1 and 2, while charges from quantum chemical calculations were used in model 3; averaging over an MD trajectory was employed in model 2.

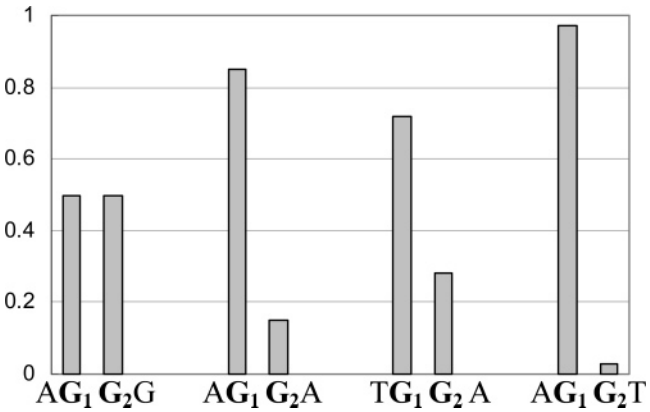

Figure 1. Hole charge distribution in sequences 5′−X-GG-Y-3′ calculated without solvation and reorganization effects ($\sigma = 0$).

potential of several $(GC)_n$ sequences embedded in AT stacks.[22] ΔE^{solv} for models with a hole localized on a single GC and a hole delocalized over two GC pairs from ref 22 are given in Table 3 along with derived values of ζ. As expected, ΔE^{solv} decreases considerably, by ~0.4 eV, with delocalization of the charge. As seen from Table 3, the solvation energies are quite sensitive to a model used in the calculation. However, the parameter ζ is rather robust, and $\zeta = -0.80$ eV appears to be a reasonable estimation.

For convenience, instead of negative quantities ρ and ζ in eq 5, we will use a positive parameter $\sigma = -(\rho + \zeta)$ that represents both the internal reorganization and solvation effects. Finally, Δq is given by

$$\Delta q = \frac{\Delta\epsilon^0 - \sigma\Delta q}{\sqrt{(\Delta\epsilon^0 - \sigma\Delta q)^2 + 4V_{12}^2}} \qquad (6)$$

The reference value of the parameter σ is 1.16 eV.

Results and Discussion

Effect of Adjacent Base Pairs. Let us consider the charge distribution in three sequences 5′-A-G_1G_2-G-3′, 5′-A-G_1G_2-A-3′, 5′-T-G_1G_2-A-3′, 5′-A-G_1G_2-T-3′. $\Delta\epsilon^0$ estimated for these systems is equal to −0.001, 0.131, 0.106, and 0.264 eV (Table 1). If $\sigma = 0$ (solvation and internal reorganization terms are neglected), then the calculated charge distributions (Figure 1) are very similar to the results published recently.[21] As expected, delocalization of the hole is quite sensitive to the nature of the base pair on the 3′ side. The results also match well with the experimental probability of cleavage.[5,6,16−18] However, two important terms have not been accounted for.

Reorganization and Solvation Effects. Let us consider a sequence 5′-A-G_1G_2-G-3′ where the absolute value of $\Delta\epsilon^0$ is very small. G_2 is an insignificantly better hole acceptor than G_1, and the hole charge is equally distributed over G_1 and G_2 (Figure 1). In Figure 2, we compare the charge distributions

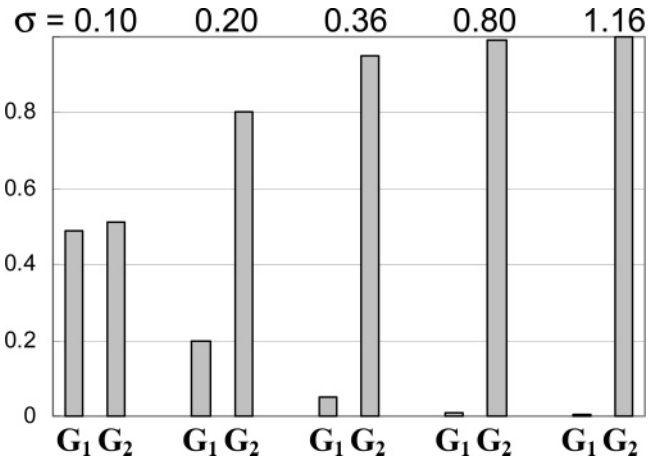

Figure 2. Effect of solvation and internal reorganization, parameter σ, on charge delocalization in 5′-A-G_1G_2-G-3′.

calculated at different values of σ ranging from 0.1 eV to its reference value of 1.16 eV. When $\sigma = 0.10$ eV, the charge distribution remains practically unchanged as compared with that shown in Figure 1 ($\sigma = 0$). However, already at $\sigma = 0.20$ eV the ratio q_2/q_1 is about 4:1. When only the reorganization term is taken into account, $\sigma = 0.36$ eV, and the hole charge is distributed as $q_1 = 0.05$ and $q_2 = 0.95$. Therefore, even in isolated duplexes (all interactions with environment are switched off), the hole states should be essentially localized. The solvation term is twice as large as the reorganization energy, $\sigma = 0.80$ eV, and therefore, a more significant localization of the positive charge is expected. Indeed, solvation forces suppress the hole delocalization for the most part part, $q_1 = 0.010$ and $q_2 = 0.990$. When both effects are accounted for, $\sigma = 1.16$ eV, $q_1 = 0.005$, and $q_2 = 0.955$. Thus, the solvation and internal reorganization effects control the charge distribution between adjacent guanine bases in DNA leading to states with a hole localized to individual Gs. It is appropriate at this point to consider whether this result is robust. From eq 6, we can derive that if

$$\left|\frac{\sigma}{V_{12}}\right| > 5 \qquad (7)$$

then the charge localized to an individual G in GG and GGG hole traps will be larger than 0.95 independent of $\Delta\epsilon^0$ (localization of the hole charge increases with $|\Delta\epsilon^0|$). The condition in eq 7 is also met for the largest value of electronic coupling from Table 2, $V_{12} = 0.20$ eV, and the reference value of $\sigma = 1.16$ eV. Although DNA configurations for which the condition in eq 7 does not hold should exist, such events appear to be rare and cannot change the overall picture. Kurnikov et al. predicted the hole states to be one to three base pairs in length.[22] Our model gives more localized hole states because the solvation effects are included in the Hamiltonian. Also the internal reorganization energy leads to additional stabilization of states with the confined hole charge.

It should be emphasized that our conclusion on localization of radical cation states does not imply that a hole will be always localized to G_2 in 5′-A-G_1G_2-G-3′ or to G_1 in 5′-A-G_1G_2-T-3′. Indeed, in the duplex 5′-A-G_1G_2-G-3′ the energy difference of two states, 5′-A-$G_1G_2^+$-G-3′ and 5′-A-$G_1^+G_2$-G-3′, where the hole is confined to G_2 and G_1, respectively, is equal to the difference of oxidation potentials of G_2 and G_1 ($\Delta\epsilon^0$). This is because in both states the solvation and reorganization terms are equal and cancel each other in eq 2 ($\Delta r = 0$, $\Delta s = 0$). Since $\Delta\epsilon^0 = -0.001$ eV is much smaller than kT, both states

are expected to be equally populated. Actually the distribution of localized radical cation states within GG and GGG traps is essentially determined by electrostatic potentials created by the surroundings. The effects of adjacent base pairs have been already accounted for. Schuster and co-authors showed that the energetics of an electron hole state in DNA is strongly affected by the configuration of neighboring sodium ions. Because of that, charge transfer in DNA depends on the probability of forming certain ion configurations that are effective in changing the hole density over the duplex DNA.[33,34] A combined quantum mechanics/molecular dynamics study[35] has demonstrated that the dynamics of water molecules strongly dominate the $\Delta\epsilon^0$ fluctuations. The standard deviation of $\Delta\epsilon^0$ due to structural fluctuations of polar surroundings is found to be about 0.3 eV for neighboring base pairs. In fact, fluctuations of $\Delta\epsilon^0$ are large enough to render electron hole transfer from G^+ to A energetically feasible.[35] Thus, the external electrostatic potential may essentially affect the position of a localized hole in DNA.

In contrast with previous calculated results, we conclude that radical cation states in DNA sequences 5′-X-GG-Y-3′ are localized to single Gs because of the substantial solvation and reorganization effects, $\sigma > 5|V_{12}|$. Ignoring these terms may lead to an incorrect picture of hole delocalization in DNA stacks.

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