# Hole Transfer and Differential Radical Recombination in X-Irradiated Doped Crystalline DNA Model Systems

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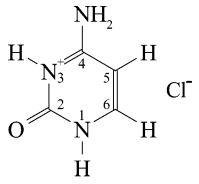
Radiation induced hole transfer and differential recombination of radicals at room temperature and lower temperatures (77 and 12 K) have been studied in crystals of cytosine·HCl doped with 5-methylcytosine·HCl (doping level 0.25−1.1 mol %). The main oxidation product stabilized in the doped crystals at room temperature is an allylic radical, called the 3αH radical, which is formed in the 5-methylcytosine dopant by net H-abstraction from the methyl group. This radical has previously been observed in various crystalline cytosine nucleosides and nucleotides shown to contain 5-methylated impurities, and it is of interest to investigate why this radical is formed in disproportionately large yields. Two effects are important in this respect. First, the 3αH radical in the present system is far less prone to recombination than the initially formed cytosine radicals, rendering the relative yield of this radical much greater than expected from the concentration of the dopant in the crystals. Second, as 5-methylcytosine has a lower ionization potential than cytosine, the 3αH radical may in addition be formed by hole transfer from oxidized cytosine to 5-methylcytosine followed by deprotonation at the methyl group. A simple model is presented which isolates the effect of such hole transfer on the relative radical yields from the effect of differential recombination. On the basis of the experimental data, and according to this model, the 3αH radical most probably is formed by fast hole transfer and radical trapping upon irradiation at room temperature. At lower irradiation temperatures the model predicts that the 3αH radical is not the dominant oxidation radical in crystalline 5-methylcytosine.

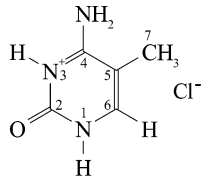
## Introduction

The selective distribution of trapped radiation induced radicals in DNA is largely a result of electron and hole transfer from initial sites to energetically deeper traps and differential decay of different radical species.[1,2] The stabilizing of radicals is mainly due to reversible and irreversible protonation/deprotonation reactions, which depend on properties such as molecular packing[2] and the acidity/basicity of the ionic radicals and their surroundings.[3,4] Some EPR studies of charge transfer in DNA and crystalline model systems have been based on introducing into the system known concentrations of intercalators, capable of scavenging migrating excess electrons or holes.[5−10] The relative yield of intercalator radicals may then be used to estimate the migration distances. One potential problem is, however, related to distinguishing between the effects of differential recombination and electron/hole transfer to the intercalator. This becomes especially pronounced for samples studied at ambient temperatures or during thermal annealing, as different radical products generally decay at different temperatures.[2,11] In this paper a simple model is outlined that makes it feasible to isolate the contribution of hole/electron transfer to the radical yields. This model is applied to a system where the effect of differential recombination is substantial both upon irradiation at room temperature and at lower temperatures (12 and 77 K). The system consists of crystalline cytosine hydrochloride (C·HCl) (structure 1 below) doped with 5-methylcytosine hydrochloride (5MC·HCl) (structure 2).

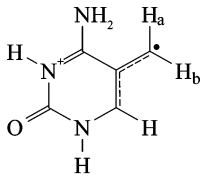
This system is studied for several reasons: In various irradiated crystalline cytosine nucleosides and nucleotides a radical has been observed,[12−15] sometimes in considerable concentrations, that is believed to be formed in 5-methylated cytosine impurities appearing in commercial supplies of cytosine derivatives (at tenths of a percent concentration or less) when they are prepared from natural products, as well as in crystals.[15,16] This radical (structure 3 below) exhibits spectroscopic characteristics similar to those of the allylic-type radical formed in thymine, formed by net H-abstraction from the thymine methyl group.[17−19] Because of anisotropic hyperfine couplings to three α-protons, the radical is called the 3αH radical.



*Structure 1*
**Cytosine·HCl (C·HCl)**



*Structure 2*
**5-methylcytosine·HCl (5MC·HCl)**



*Structure 3*
**The 3αH radical**

The irreversible deprotonation at the methyl group should render this radical less exposed to recombination as compared

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to other radicals formed in this system.[20,21] It is therefore of interest to investigate whether the disproportionately large concentrations of this radical in these nucleotides in addition are resulting from a transfer of holes to 5MC-containing impurities, as the ionization potential for 5MC is lower than that for C.[16] This is also of relevance to DNA, in which several percents of the cytosines are 5-methylated.[22] Some portion of an allylic radical that has been observed in DNA, and which is ascribed to be formed in thymine,[11] could hence actually be a cytosine radical.

## 2. Experimental Procedures

EPR spectroscopy was used to measure relative radical yields in crystalline and polycrystalline samples of C·HCl doped with varying amounts 5MC·HCl at 12, 77, and 295 K. The molar doping level was determined by proton NMR spectroscopy. The experimental procedures including preparation of samples, NMR measurements, instrumentation, X irradiation to doses up to 140 kGy, X-band EPR measurements, and computational techniques were as described previously.[23−26] Identification of radical structures and calculation of their hyperfine coupling tensors were made in a recent ENDOR study.[26] The EPR spectra of the samples were recorded at a given time after irradiation, and the radical yields appeared to remain stable for at least several hours. The relative radical yields were determined by double integration of the corresponding EPR spectra, recorded with an $Mn^{2+}$/MgO reference independently mounted in the cavity at 295 and 77 K, weighted for differences in sample masses. The contribution to the different spectra from the only identified oxidation product in 5MC, the 3αH radical, was estimated by reconstructing experimental EPR spectra using benchmark spectra of various components in a fitting procedure as described previously.[26,27]

It is assumed that the 5MC molecule takes the place of a cytosine molecule without significantly changing the orientation of the base in the lattice. This assumption was confirmed by data analysis from the previous work.[26]

## 3. Model for Detecting Hole Transfer

The model described below concerns hole transfer, but it is equally applicable for transfer of excess electrons. The system under consideration may be any ordered molecular assembly where some of the host molecules (D) have been exchanged with dopant molecules (A) acting as hole (or electron) acceptors. In the present work, molecular single crystals have been used, and in the following, *crystals* have thus been used to designate the samples. In the following account it is assumed that a host molecule (D) and an acceptor (A) have the same probability of being oxidized by the ionizing radiation and (for simplicity) that the acceptors A have the same probability of trapping excess electrons as D. It is further assumed that the dopant does not alter the crystal structure.

In this system radiation induced holes (electron vacancies) may transfer from initial-site donor radicals ($D^{\bullet+}$)[28] to nonradical acceptors (A), yielding the oxidation products $A^{\bullet+}$. This type of transfer is distinguished from transfer of holes due to recombination processes where the acceptor sites are also radicals. The following *processes* are proposed for formation of the oxidation products $A^{\bullet+}$:

I: $A^{\bullet+}$ may be formed by the ionizing radiation.

II: $A^{\bullet+}$ may be formed by holes being transferred from $D^{\bullet+}$ to A and subsequently trapped by the latter. This process, which is the process of main interest in the present work, is assumed to be promoted by a lower ionization potential for D than for A.

III: During the recombination of the $D^{\bullet\pm}$ (ref 28) radicals, migrating holes may be trapped[29] by A and form $A^{\bullet+}$. This would temporarily or permanently terminate the migration of the holes, which otherwise, in the absence of A, would have recombined with other D radicals. The migration of these holes is thus not caused by the presence of A.

To investigate the efficiency of process II, the enhancement of the yield of $A^{\bullet+}$ due to this process only must be isolated. The fraction of $A^{\bullet+}$ relative to the total amount of oxidation products, $f = [A^{\bullet+}]/([A^{\bullet+}] + [D^{\bullet+}])$, is initially equal to the molar doping level, which is denoted by $d$. Hole transfer after the initial ionization (process II) makes $f > d$. However, the relative yield of $A^{\bullet+}$ is also increased when the $A^{\bullet+}$ species are less exposed to recombination than the $D^{\bullet+}$ species. Process III will in that case also enhance the yield of $A^{\bullet+}$. The total radical yield will moreover be greater in doped crystals than in undoped crystals (and may be further increased by reduction products that are prevented from recombining with holes being trapped as $A^{\bullet+}$). Hence, a relative yield of $A^{\bullet+}$ greater than the doping level, $f > d$, does not necessarily demonstrate that hole transfer by process II has occurred. Instead, one must investigate the decrease of the yield of $D^{\bullet+}$ in doped crystals, relative to the yield of $D^{\bullet+}$ in undoped crystals. This fraction $F$ is defined as

$$F \equiv \frac{N_0^{D^{\bullet+}} - N_d^{D^{\bullet+}}}{N_0^{D^{\bullet+}}} \tag{1}$$

where $N_d^{D^{\bullet+}}$ and $N_0^{D^{\bullet+}}$ are the yields of $D^{\bullet+}$ in doped and undoped crystals, respectively. As will be explained below, $F$ can be used to estimate the effective range of the hole migration when the following proposition is true: The radicals $D^{\bullet+}$ in doped crystals that are not involved in process II and the radicals $D^{\bullet+}$ in undoped crystals decay in the same proportion. This proposition may be justified by the assumption that hole transfer by process II is independent of recombination processes and noting that formation of $A^{\bullet+}$ by process III may be considered as a mode for decay of $D^{\bullet+}$. Also, it can be assumed that the mobility of the recombining charges (holes/electrons) is not affected by the dopant when the doping level is sufficiently small.

The numerator in eq 1 describes the reduction in $D^{\bullet+}$ due to the presence of A, and $F$ describes the reduction relative to the yield of $D^{\bullet+}$ in the undoped crystals. The proposition above entails that at least some of the $A^{\bullet+}$ formed by process II, at any instant during the decay process of $D^{\bullet+}$, result in an increase of $F$. Prior to any hole transfer, $F$ is equal to the doping level $d$. Hole transfer by process II thus makes $F > d$ and enhances the yield of $A^{\bullet+}$ by the factor $F/d$.

In many cases it will be difficult to determine $F$ by application of eq 1, since $D^{\bullet+}$ may be hard to isolate spectroscopically (e.g. by using EPR). When the spectroscopic properties of the $A^{\bullet+}$ radicals differ considerably from those of the $D^{\bullet\pm}$ radicals, the yield of $A^{\bullet+}$ may be more easily quantified. $F$ may then be determined by using the yield of $A^{\bullet+}$ together with the total radical yields of a doped and an undoped crystal, which in the following are denoted $N_d$ and $N_0$, respectively. The amount of $A^{\bullet+}$ in a doped crystal is further given as $N_d^{A^{\bullet+}}$. The amounts of oxidation products in a doped and an undoped crystal can then be expressed as $N_d^{D^{\bullet+}} + N_d^{A^{\bullet+}} = aN_d$ and $N_0^{D^{\bullet+}} = bN_0$, respectively, where $a, b \in [0, 1]$. If the $A^{\bullet+}$ radicals are more stable than the $D^{\bullet+}$ radicals, it follows that $a \geq b$. When the total amount of $A^{\bullet+}$ within $N_d$ is given as $pN_d$ ($p \in [0, 1]$), the numerator in eq 1 can be expressed as $N_0^{D^{\bullet+}} - N_d^{D^{\bullet+}} = bN_0 - (a - p)N_d$. The fraction $F$ is then expressed as

$$F = \frac{bN_0 - (a-p)N_d}{bN_0} \geq \frac{N_0 - (1-p/a)N_d}{N_0} \quad (2)$$

(since $a \geq b$). When the radicals decay predominantly by electron/hole recombination, then $a, b \cong {}^1/_2$ and

$$F \cong \frac{N_0 - (1-2p)N_d}{N_0} \quad (3)$$

The expression contains now only quantities that are feasible to determine.[30]

An expression for the upper and lower limits of the effective range of the hole transfer is given in the following, in accordance with the analysis made by Sevilla and co-workers,[9,10] for a random distribution of acceptors A and donors $D^{\bullet+}$ in the crystals.[31] The capability of the acceptors to trap holes can be defined to be as if the acceptors are surrounded by a scavenging volume having the property that those, and only those, holes that are formed within such volumes migrate to the acceptors. (This definition can be applied independent of the hole transfer mechanisms.) Alternatively, this scavenging volume can be considered as a volume around the holes with the corresponding property of hole transfer to acceptors being present within the volume. The scavenging volume contains a number of $M$ molecules, including the molecule where the hole is originally formed. When the concentration of A in the crystals is much greater than the concentration of $D^{\bullet+}$, the probability that at least one acceptor is among the $M$ molecules for an arbitrary chosen hole escaping recombination is given by $1 - (1-d)^M$, where $d$ is the doping level. This probability is then approximately equal to the fraction $F$, that is

$$F \cong 1 - (1-d)^M \quad (4)$$

Two extremes for the range of the hole transfer can now be given. If the holes are confined to migrate in only one dimension, for example along one preferred path in the system, the number of molecules constituting the scavenging volume is given as

$$M = 2r + 1 \quad (5)$$

where $r$ is the range of the transfer expressed in intermolecular distances. This yields an upper limit of the transfer range. A lower limit is obtained when the volume constitutes a sphere with radius $r$, which means that the holes can migrate in three dimensions with equal probability of transfer in all directions. This sphere covers $M$ molecules; that is, $(4\pi/3)r^3 = (V_m M)/N_A$, where $V_m$ is the molar volume and $N_A$ is Avogadro's constant. This isotropic range is then expressed as

$$r = \left(\frac{3V_m M}{4\pi N_A}\right)^{1/3} \quad (6)$$

Generally, the probability for transfer depends on the direction relative to the crystal structure, as the factors facilitating hole transfer such as intermolecular distances and electronic orbital overlapping are anisotropic.

## Results

Figure 1 shows dose−yield curves obtained at room temperature for pellets made of pure C·HCl, C·HCl mechanically mixed with 1 mol % 5MC·HCl, pure crystalline 5MC·HCl, and crystalline C·HCl doped with 0.18 mol % 5MC·HCl. It appears that small amounts of 5MC·HCl have little effect on the total radical yield when mechanically mixed with C·HCl. When 5MC·HCl is doped into the crystal lattice of C·HCl, the radical yield increases considerably, indicating that intermolecular processes take place in the crystals following irradiation.

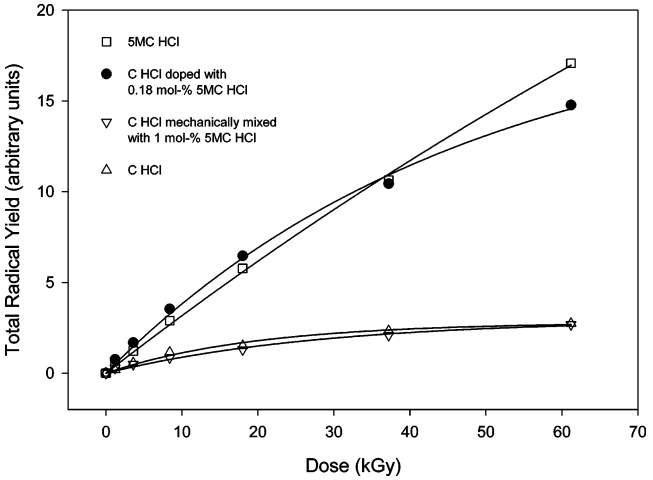



**Figure 1.** Total radical yield at 295 K as a function of dose for pellets made from various crushed crystals or polycrystalline materials as indicated. The solid lines were obtained by fitting the data to the function $C = C_\infty(1 - e^{-D/D_{37}})$, where $C$ is the radical concentration, $D$ is the dose, $C_\infty$ is the saturation level of the radical concentration, and $D_{37}$ is the dose at which the radical concentration is 37% away from saturation (the fitting parameters are not presented, since they are not used in this work.)

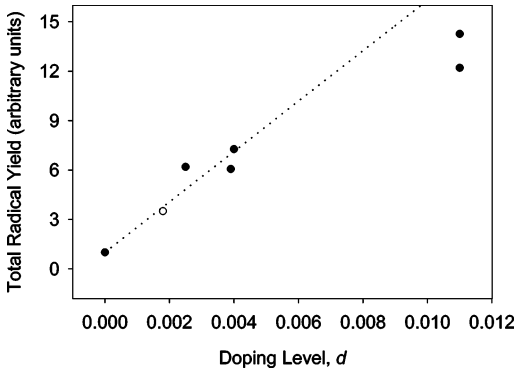



**Figure 2.** Total radical yields in pellets made from crushed crystals of C·HCl doped with 5MC·HCl, X-irradiated (9 kGy) and measured at 295 K. The value marked as an open circle is obtained from the dose−yield curve in Figure 1. The dotted line illustrates that the increase in radical yield deviates from linearity for higher doping levels. The units for the radical yields are the same as those in Figure 1.

Figure 2 shows the total radical yield at room temperature for pellets made from crystals of C·HCl doped with varying amounts of 5MC·HCl after a dose of 9 kGy, a dose in the linear part of the dose−yield curves in Figure 1. The data suggest an approximately linear increase of the radical yield at small doping levels (dotted line) and that this increase eventually declines. The major part of the radicals associated with 5MC in the crystals is the oxidation products being referred to as the 3αH radicals (structure 3),[26] which correspond to the $A^{\bullet+}$ species in the model description. The increase in total radical yield with the doping level implies that the 3αH radicals are far more stable than the cytosine radicals initially formed. The fraction of the 3αH radicals formed in the crystals was estimated in the previous work and, as shown in Figure 3, it apparently approaches 0.5 asymptotically with the doping level (the solid line is discussed below). This suggests an even distribution of reduction and oxidation products in the crystals and that the

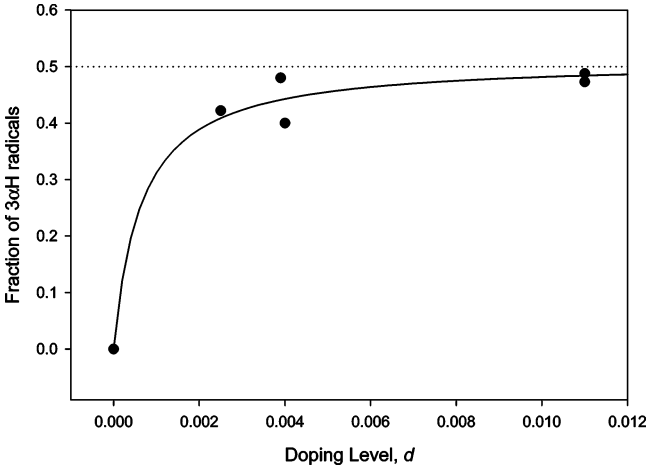



**Figure 3.** Fraction ($p$) of 3αH radicals of total radical yield in crystals of C·HCl doped with various amounts of 5MC·HCl, X-irradiated and measured at 295 K. The solid line is obtained as described in the text.

**TABLE 1: Doping Levels ($d$), Fraction[a] of 3αH Radicals ($p$), the Ratio of Total Radical Yields in Doped Crystals vs an Undoped Crystal ($N_d/N_0$), and the Fraction $F$ as Calculated Using Eq 3, for Crystals of C·HCl Doped with 5MC·HCl, X-Irradiated (9 kGy) and Measured at 295 K**

| doping level (%) | % 3αH | $N_d/N_0$ | $F$ |
|---|---|---|---|
| 0.25 | 42.2 (3) | 6.2 | 0.033 |
| 0.39 | 48.0 (4) | 6.1 | 0.756 |
| 0.40 | 40.0 (4) | 7.3 | −0.460 |
| 1.1 | 48.8 (4) | 12.2 | 0.707 |
| 1.1 | 47.3 (4) | 14.3 | 0.228 |

[a] Uncertainties obtained from the reconstruction of spectra are given in the last digit of the quoted values.

initially formed radicals predominantly decay by electron/hole recombination. This is also supported by the observation of the large yield (>30% of the total radical yield) of a cytosine reduction product, known as the 5-yl radical,[32] in the doped crystals.[26] These latter radicals are formed and stabilized in excess assumedly because oxidation products ($D^{\bullet+}$) that normally would recombine with the reduction products instead are stabilized as 3αH radicals ($A^{\bullet+}$).

The fraction $F$ (eq 1) can then be estimated using eq 3. The values of $F$ along with the relative amounts of the 3αH radical ($p$) and the radical yields for the doped crystals ($N_d$) relative to the yield in the undoped crystal ($N_0$) are shown in Table 1. The large, inconsistent variation of $F$ reflects the uncertainties in the parameter values (as is evident from Figures 2 and 3). Thus, the following analysis must be regarded as tentative but, nevertheless, illustrative for the potential use of the model described. The data in Table 1 seem to indicate that $F > d$ (doping level), so that a hole transfer from oxidized C to 5MC takes place in the crystals. Fitting eq 4 to the values of $F$ gives for the number of $M$ molecules constituting the scavenging volume surrounding the acceptors (the 5MC bases) $M = 51$. Due to the large scatter in the present data, this number is very uncertain (>50%). Combining eqs 3 and 4 gives for the relative amount of the 3αH radicals ($p$ in eq 3)

$$p = {}^1/_2 - \frac{(1-d)^M N_0}{2N_d} \qquad (7)$$

Assuming that the total radical yield is less than or equal to the dotted line in Figure 2, then $N_d/N_0 \leq 1530d + 1$, approximately, which when inserted into eq 7, with $M = 51$, gives the solid line in Figure 3. Good agreement with the experimental data is obtained.

**TABLE 2: Doping Levels ($d$), Fraction[a] of 3αH Radicals ($p$), and the Ratio of Total Radical Yields in Doped Crystals vs an Undoped Crystal ($N_d/N_0$) for Crystals of C·HCl Doped with 5MC·HCl, X-Irradiated (140 kGy) and Measured at 77 K**

| doping level (%) | % 3αH | $N_d/N_0$ |
|---|---|---|
| 0.03 | 3.4 (1) | 1.15 |
| 0.29 | 9.0 (2) | 2.4 |
| 0.56 | 11.9 (3) | 2.6 |

[a] Uncertainties obtained from the reconstruction of spectra are given in the last digit of the quoted values.

When it is assumed that the hole transfer takes place in one dimension only, eq 5 gives for the upper limit of the transfer range $r = 25$ intermolecular distances. If this transfer occurs within stacks (see below) of cytosine bases, then this range corresponds to ∼8.2 nm, as the average distance between neighboring bases in a stack is 0.327 nm.[33] The density of C·HCl is $1.57 \times 10^3$ kg/m$^3$, which gives a molar volume $V_m \cong 94.0 \times 10^{-6}$ m$^3$/mol. The lower limit of the hole transfer is given by eq 6 for transfer in three dimensions with isotropic transfer probability and amounts to $r \cong 1.2$ nm.

The only radical associated with 5MC identified by ENDOR at 12 K was the 3αH radical.[26] However, when assuming equal amounts of oxidation and reduction products in the crystals, the relative amounts of the 3αH radical were not sufficient, even after X irradiation and measurements at 77 K, to confirm that a hole transfer by process II had taken place in the crystals according to eq 3. This can be seen from Table 2, where the fraction of 3αH radicals, relative radical yields, and doping levels for three samples after a dose of 140 kGy[34] are given. These parameter values give negative values for $F$. In order that $F \geq d$, the amount of 5MC radicals missing must make up at least 20% of the total radical yield for doping levels of 0.3−0.6 mol %. This seemed also to be the case at 12 K, even though the cavity used at this temperature was not equipped with a reference sample so that the radical yields for doped and undoped samples were not easily compared. These observations indicate that the 3αH radical is not the dominant radical formed in 5MC at low temperatures. This is also supported by previous EPR studies of 5MC.[35−37] Upon thermal annealing to 295 K, the EPR spectra (powder and single-crystal spectra) of doped crystals were virtually identical to spectra of the samples irradiated at 295 K, although with a much smaller signal-to-noise ratio. It is interesting to note that the presumably dominant radical in 5MC at low temperatures,[38] while almost certainly not being irreversibly deprotonated, is considerably more stable than the cytosine radicals at these low temperatures.

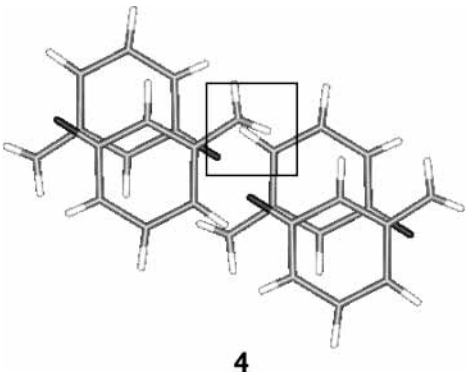
## Discussion

The room temperature data suggest that the 3αH radical is formed by a transfer of holes from radiation oxidized C to 5MC, followed by deprotonation at $-CH_3$. This transfer is presumably due to a lower ionization potential for 5MC than for C.[16] Whether this radical is also formed by capture of migrating holes during recombination processes (process III in the model section) was not possible to confirm from the present experiments. The 3αH radical was further shown to be far more stable than the C radicals, both at 295 and 77 K and most probably at 12 K. The high stability of this radical is most likely due to the irreversible deprotonation at $-CH_3$. To compare the efficiencies of 5MC and C in trapping oxidative damage (in the crystal lattice of C·HCl), the amount of the 5MC radicals that has been formed by the irradiation must be known. When assuming equal

amounts of oxidation and reduction products in the crystals, and denoting the total amount of radicals initially formed by $N_i$, the fraction of cytosine oxidation radicals in an undoped crystal escaping destruction is $N_0/N_i$. The total amount of the 3αH radicals that has initially been formed by the irradiation can be expressed as $dN_i/2$. If this quantity of 3αH radicals alone is responsible for the increase of the oxidative radical yield, compared to that of an undoped crystal, then the fraction of these initially formed 3αH radicals escaping destruction is $^1/_2(N_d - (1 - d)N_0)/(dN_i/2)$. The 3αH radicals are then more efficiently trapped than the cytosine oxidation radicals by a factor of $(N_d - (1 - d)N_0)/(N_0d)$. In the present system at 295 K this amounts to a factor of $>10^3$ for the radical yields in Figure 2. Another limit would be obtained if the hole transfer takes place immediately after the initial formation of the holes, before any recombination is possible. The fraction of the 3αH radicals escaping destruction in that case is $pN_d/(FN_i/2)$. This amounts to the 3αH radicals having a higher probability of being trapped than the cytosine oxidation radicals by a factor of $2pN_d/(FN_0)$, which at 295 K probably lies between 20 and 100. This factor is reduced if some of the 3αH radicals have been formed by process III. The dose−yield curves for pure 5MC·HCl and C·HCl in Figure 1 indicate that this latter limit is more realistic and, consequently, that the trapping process (hole transfer and deprotonation) is fast at room temperature.

It is thus probable that the observation of the 3αH radical in the irradiated crystalline nucleoside cytidine and the nucleotides 3′-CMP and 5′-dCMP[12−15] is due to 5-methylated impurities in these systems[15,16,26] and that both hole transfer and differential recombination are responsible for the relatively large yields of this radical. (Similar processes may also be responsible for the 3αH radical in crystalline 2-thiouracil.[39]) These results may have consequences for DNA itself, which contains several percents of 5-methylated cytosine.[22] Oxidized 5MC apparently deprotonates easily at the methyl group. 5MC, having a lower ionization potential than C[16] and (consequently) thymine,[40] may then act as a sink for oxidative damage, similar to guanine, and the irreversible deprotonation consolidates the damage. As has been pointed out by Close,[16] some of the thymine allyl radicals believed to be formed in DNA[11] could in fact be the cytosine 3αH radical, which gives almost the same EPR spectrum.

The hole transfer in the present system at 295 K is conceivably a combination of single-step tunneling and multistep hopping[41−43] and may be expected to take place in several directions, as is the case in DNA.[10,44] Due to the ordered structure, the probability for transfer may be anisotropic. In the crystal lattice of C·HCl, stacking of bases occurs only within pairs of bases and not between these pairs, with planar distances of 0.331 nm between the stacked bases and 0.323 nm between the nonstacked neighboring bases.[33] This is illustrated in structure 4, where bases in two neighboring pairs are viewed along the ring normal. However, as outlined in structure 4, overlapping of molecular orbitals may occur between C5 and N4 in a neighboring nonstacked molecule, thus providing a preferred path for the hole transfer via the $\pi$-orbitals. The cytosine oxidation product observed at 12 K also contained spin density at C5 (∼0.6) and at N4 (∼0.2).[26]



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Whether hole transfer takes place at lower temperatures (77 and 12 K) was not possible to determine. More knowledge of the dominating 5MC oxidation products at these temperatures is needed for that purpose.

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(28) In this nomenclature, $A^{\bullet+}$ and $D^{\bullet+}$ are radical species, and the + and − signs are used only to differentiate between oxidation and reduction products and are not indicators of the actual charge of the radical.

(29) The holes that form $A^{\bullet+}$ in this process are presupposed to migrate through multistep hopping.

(30) The possibility that the $A^{\bullet+}$ species are less stable than the $D^{\bullet+}$ species should be commented on. This means that $N_d < N_0$. Hole transfer by process II may then cause the total radical yield to further decrease. This, of course, presupposes that the hole transfer takes place before the radicals recombine. Following eq 1 and assuming equal amounts of oxidation and reduction products in the doped and undoped crystals (for simplicity), the amount of $D^{\bullet+}$ in doped crystals is $N_d/2 - pN_d$. (The total yield of $A^{\bullet+}$ is still given as $pN_d$.) The reduction of the yield of $D^{\bullet+}$ in the doped crystals is then $N_0/2 - (N_d - 2pN_d)/2$, entailing that $F$ is still expressed by eq 3.

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