

- [8] S. Söhnchen, S. Lukas, G. Witte, *J. Chem. Phys.* **2004**, in press.  
 [9] H. Oji, R. Mitsumoto, E. Ito, H. Ishii, Y. Ouchi, K. Seki, T. Yokoyama, T. Ohta, N. Kosugi, *J. Chem. Phys.* **1998**, *109*, 10409.  
 [10] H. Ågren, O. Vahtras, V. Carravetta, *Chem. Phys.* **1995**, *196*, 47.  
 [11] C. Mainka, P. S. Bagus, A. Schertel, T. Strunskus, M. Grunze, Ch. Wöll, *Surf. Sci.* **1995**, *341*, L1055.  
 [12] K. Weiss, S. Gebert, M. Wühh, H. Wadepohl, Ch. Wöll, *J. Vac. Sci. Technol.* **1998**, *A16*, 1017.  
 [13] L. G. M. Pettersson, H. Ågren, Y. Luo, L. Triguero, *Surf. Sci.* **1998**, *408*, 1.  
 [14] E. Umbach, K. Glöckler, M. Sokolowski, *Surf. Sci.* **1998**, *404*, 20.  
 [15] P. G. Schroeder, C. B. France, J. B. Park, B. A. Parkinson, *J. Appl. Phys.* **2002**, *91*, 3010.  
 [16] T. Minakata, H. Imai, M. Ozaki, K. Saco, *J. Appl. Phys.* **1992**, *72*, 5220.  
 [17] P. Ruffieux, O. Gröning, M. Biemann, C. Simpson, K. Müllen, L. Schlapbach, P. Gröning, *Phys. Rev. B* **2002**, *66*, 073409.  
 [18] J. Cornil, H. Ph. Calbert, J. L. Brédas, *J. Am. Chem. Soc.* **2001**, *123*, 1250.  
 [19] G. Loepf, S. Vollmer, G. Witte, Ch. Wöll, *Langmuir* **1999**, *15*, 3767.  
 [20] P. Fouquet, G. Witte, *Surf. Sci.* **1998**, *400*, 140.  
 [21] R. Denecke, P. Väterlein, M. Bäessler, N. Wassdahl, S. Butorin, A. Nilsson, J.-E. Rubensson, J. Nordgren, N. Martensson, R. Nyholm, *J. Electron Spectrosc. Relat. Phenom.* **1999**, *971*, 101–103.

Received: June 25, 2003 [Z 892]

Revised: September 29, 2003

## 4'-Pivaloyl Substituted Thymidine as a Precursor for the Thymyl Radical: An EPR Spectroscopic Study\*\*

Olav Schiemann,<sup>\*,[a]</sup> Emiliano Feresin,<sup>[a]</sup> Thomas Carl,<sup>[b]</sup> and Bernd Giese<sup>[b]</sup>

Hole migration through DNA has been extensively debated over the past three decades<sup>[1]</sup> but just within the last three years the results of studies on well-defined photoexcitable donor–DNA–acceptor systems<sup>[2]</sup> has led to a mechanistic picture, which accounts for distance, base sequence and energy dependences.<sup>[3]</sup>

[a] Priv. Doz. Dr. O. Schiemann, E. Feresin  
 Institute of Physical and Theoretical Chemistry  
 J. W. Goethe-University, Marie Curie-Strasse 11  
 D-60439 Frankfurt/Main (Germany)  
 Fax: +49-69-798-29-404  
 E-mail: o.schiemann@prisner.de

[b] T. Carl, Prof. B. Giese  
 Department of Chemistry  
 University of Basel  
 St. Johanns-Ring 19, CH-4056 Basel, Switzerland.

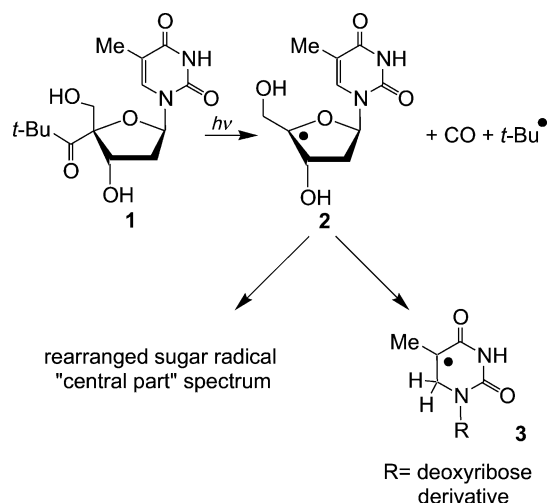
[\*\*] EPR = electron paramagnetic resonance.

Supporting information for this article is available on the WWW under <http://www.chemphyschem.org> or from the author.

On the contrary, still less is known about electron transfer (ET) in DNA.<sup>[4]</sup> In the beginning, excess electrons were generated in DNA in an unselective way by using high energy radiation.<sup>[5]</sup> Therefore, Sevilla et al. had to use statistical models in their electron paramagnetic resonance (EPR) studies to deduce a distance dependence for the ET rate of  $\beta = 0.9 \text{ \AA}^{-1}$ .<sup>[6]</sup> However, as in the case of the hole-transfer studies, oligonucleotides with known donor–acceptor distances and complementary analytical and spectroscopic techniques are required for a complete understanding of the ET in DNA.

Recently, systems were established which fulfill this requirement, for example, the repair of a thymine–thymine–dimer through an excited flavine by Carell and co-workers<sup>[7]</sup> or the observation of an electron transfer from 2-aminopurine to a next neighbour thymine base by Zewail and co-workers.<sup>[2e]</sup> More detailed studies were reported by Fiebig, Wagenknecht and co-workers on a pyrenyl-modified deoxyuridine, whose excitation initiates an electron transfer to a close by thymine base,<sup>[8]</sup> and by Lewis et al. who used photoexcited singlet stilbene to reveal the dependence of the electron injection on the driving force.<sup>[9]</sup>

Here we show by means of EPR spectroscopy that UV irradiation of the 4'-pivaloyl-substituted thymidine (**1**; Scheme 1) leads to a homolytic C–C bond cleavage at the 4'-site, as

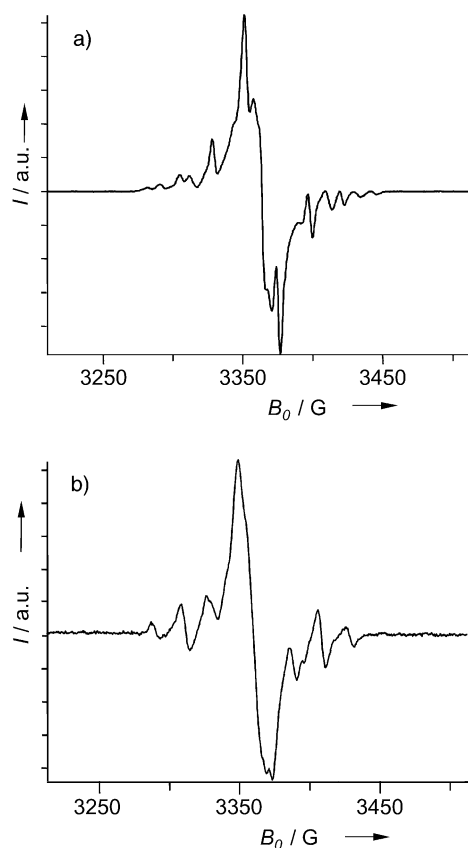


**Scheme 1.** Formation of the 4'-nucleoside radical **2** by photolysis of the 4'-pivaloylated nucleoside **1** and the subsequent formation of the thymyl radical **3** and a rearranged sugar radical.

suggested previously,<sup>[10]</sup> and subsequently to a hydrogen- or proton-coupled electron-transfer step from the first formed carbohydrate radical **2** to the thymine base. Hence, **1** or similar derivatives thereof may be used as ET initiators in DNA.

The first measurements were carried out with the pivaloylated thymidine **1** dissolved in acetonitrile. After 200 s of irradiation at 77 K the 165-G broad EPR spectrum displayed in Figure 1 a was obtained.

The photolysis of unmodified thymidine in the presence of di-*t*-butylketone only led to *t*-butyl radicals. No signal was obtained with thymine or thymidine photolyzed under the same conditions, which reveals that the radical formation is not due to

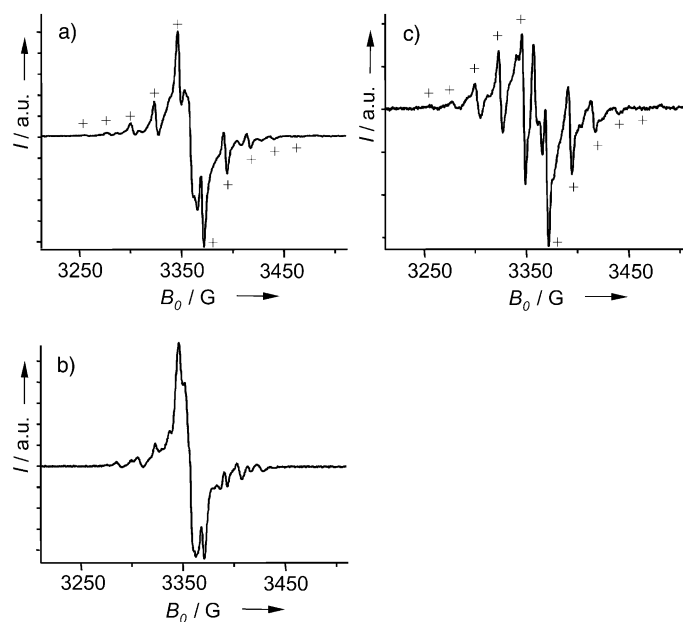


**Figure 1.** a) CW X-band EPR spectrum of a 0.12 M solution of **1** in  $\text{CH}_3\text{CN}$  irradiated and measured at 77 K. The spectrum was acquired at a microwave power of 1 mW, a modulation amplitude of 0.7 G, a receiver gain of  $2 \times 10^4$ , a conversion time of 40.96 ms and a time constant of 40.96 ms. 50 scans were accumulated. b) CW X-band EPR spectrum of the photolysis products of **1** in  $\text{H}_2\text{O}$  at 80 K using a microwave power of 1 mW.

direct UV damage of the thymine base, nor to intermolecular reactions, but to a homolytic C–C bond cleavage at the site of the pivaloyl substituent. Such a bond cleavage is known to proceed via a Norrish I-type reaction<sup>[11]</sup> and was used previously to generate hexose radicals.<sup>[12]</sup>

Power saturation measurements were then performed to get a first impression of whether all of the observed lines belong to only one or more radical species (Figure 2). Subtracting the high-power (Figure 2a) from the low-power (Figure 2b) spectrum yielded the ten-line spectrum in Figure 2c with a splitting of 22.7 G; this spectrum resembles the *t*-butyl radical spectrum known from the literature.<sup>[13]</sup> These spectra alone are not significant, nevertheless they show that the spectrum in Figure 1a is a superposition of spectra of different radicals.

Next, experiments with **1** dissolved in water were carried out to suppress the water-sensitive *t*-butyl radical, and hence to simplify the spectrum. From the spectrum in Figure 1b (recorded at 80 K) it can be seen that the ten-line spectrum of the *t*-butyl radical is almost completely suppressed, leaving a spectrum displaying eight well-resolved lines with a clear splitting of 20.4 G and an intense “central part”. No new signals from reactions with water or OH radicals<sup>[5a, 14]</sup> could be detected.

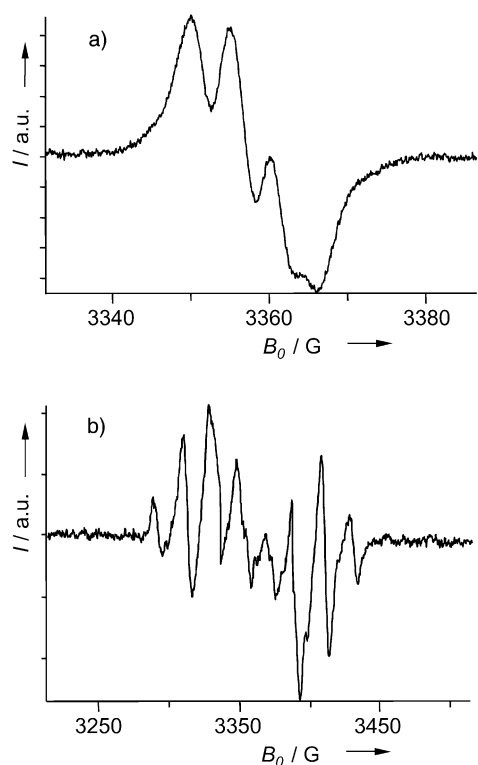


**Figure 2.** a) CW X-band EPR spectrum of **1** in  $\text{CH}_3\text{CN}$  at 77 K after 200 seconds of irradiation and using a microwave power of 15 mW. b) The same sample but using a microwave power of 40  $\mu\text{W}$ . c) 10-line spectrum (indicated by +) generated by subtraction of the low-power spectrum from the high-power spectrum, after normalising the low-power spectrum to the maximum amplitude of the high-power spectrum.

Irradiating a sample of **1** in water, not at 80 K but at 4 K, showed an EPR spectrum where only the central part of the spectrum remained. When the solvent was changed to  $\text{D}_2\text{O}$ , it was possible to narrow the line width and to resolve the central part of the spectrum, which displayed three lines with a splitting of 5 G and a shoulder. Heating this sample to 140 K in 10 K steps did not change the signal components, but decreased the line width even more to 2.5 G (Figure 3a). Above 200 K no signal was observable.

The subtraction of the central part of the spectrum in Figure 3a, which contains no contributions from the eight-line or ten-line spectra, from the spectrum in Figure 1b, yielded the pure eight-line spectrum shown in Figure 3b. This spectrum is the so called “octet-fingerprint” spectrum of the thymyl radical.<sup>[5d, 15]</sup> In previous reports, electron scavengers were used to prevent the formation of thymine radical anion or thymyl radicals.<sup>[16]</sup> Hence, the electron scavenger  $\text{K}_3[\text{Fe}(\text{CN})_6]$  was added to a solution of **1** in  $\text{H}_2\text{O}$  to check whether it is possible to suppress the eight-line spectrum in this way also at 80 K. This treatment gave a spectrum dominated by the “central part” signal, whereas the eight-line spectrum is diminished (see the Supporting Information). The “central part” spectrum again exhibits the same line pattern as the spectrum at 4 K, but it is less well-resolved.

It can be concluded from these experiments that three different radicals are generated upon irradiation of the 4'-pivaloylated thymidine **1**, which give rise to a ten-line, a eight-line and the “central part” spectrum. The ten-line spectrum shown in Figure 2c can unambiguously be assigned to the *t*-butyl radical (*t*-Bu $\cdot$ ) by comparison with spectra from the

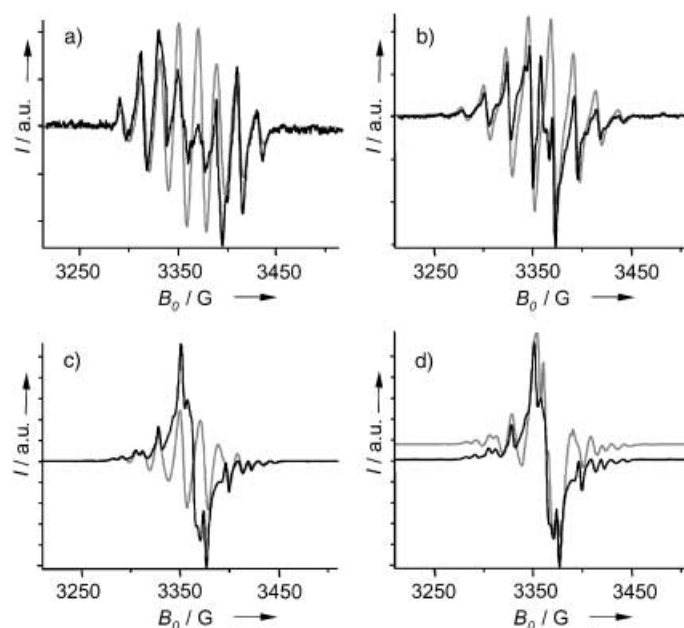


**Figure 3.** a) CW X-band EPR spectrum of the photolysis products of **1** in  $D_2O$  at 140 K after 40 s of irradiation at 4 K. The spectrum was recorded using a microwave power of 0.1 mW. b) Pure eight line spectrum obtained after subtracting the pure central part spectrum in a) from the spectrum in Figure 1a. The central part spectrum was normalised to the maximum amplitude of the spectrum in Figure 3a prior to subtraction.

literature.<sup>[13]</sup> The sensitivity to water and the saturation at high microwave power are also characteristic for the *t*-butyl radical.<sup>[17]</sup> Its formation is due to the Norrish I type cleavage (Scheme 1).

The eight-line spectrum is the typical octet-fingerprint spectrum of the thymyl radical **3**.<sup>[15]</sup> This assignment is supported by the suppression of the octet spectrum in the presence of an electron scavenger. Both spectra, the thymyl and the *t*-butyl radical spectrum, were simulated (Figure 4a,b) with the parameters given in the caption of Figure 4 matching the parameters from the literature. Adding both simulated spectra in a ratio of 1:1 (Figure 4c) and superimposing the result on the central part spectrum of Figure 3a with a ratio of 1:4 forms the total spectrum in Figure 4d, which resembles the spectrum generated by photolysis of **1** in acetonitrile very nicely. Small differences may be due to different line widths at different microwave powers. This shows that all spectral components were accounted for.

An assignment of the central part spectrum is difficult, but it is clear that this radical is not the precursor of the thymyl radical **3** and hence not the 4' sugar radical because it can not interconvert to **3** when warmed from 4 K to 200 K in 10 K steps. We assume that the 4'-nucleoside radical **2**, formed by Norrish cleavage of **1**, has two pathways, one of which leads to a rearranged sugar radical (maybe by  $\beta$ -bond cleavage or an H-atom shift) exhibiting the central part spectrum, the other one



**Figure 4.** a) Simulation (grey curve) of the spectrum of thymyl radical **3** using hyperfine coupling constants of a ( $^1H$ ) = 20.5 G for the three hydrogen atoms at the methyl group and of 37.5 G for the two methylene hydrogen atoms and a line width of 8 G. The experimental spectrum is overlaid in black. b) Simulation of the *t*-Bu $^{\bullet}$  spectrum (grey curve) using a hyperfine coupling constant of a ( $^1H$ ) = 22.7 G for the nine equivalent methyl hydrogen atoms and a line width of 6.5 G. The experimental spectrum is overlaid in black. c) Simulated sum spectrum (grey curve) obtained from a 1:1 superposition of the simulated spectrum of **3** with the *t*-Bu $^{\bullet}$  spectrum. The experimental spectrum from Figure 1 is overlaid in black. d) Simulated sum spectrum (grey curve) obtained from a 1:4 superposition of the simulated spectrum in c) with the central part spectrum of Figure 3a. The experimental spectrum from Figure 1 is overlaid in black.

yielding the thymyl radical **3** (Scheme 1). The reaction **2**  $\rightarrow$  **3** is a proton-coupled electron or hydrogen-atom transfer from the 4'-deoxyribosyl radical to the thymine base,<sup>[18]</sup> similar to the mechanism described by Hüttermann et al. for the X-ray irradiation-induced formation of the 5-yl base radicals from 5-chloro and 5-bromodeoxyuridine.<sup>[19]</sup>

Intermolecular reaction pathways leading to the formation of the thymyl radical **3** can be excluded, since a reaction between thymine and the *t*-butyl or solvent radicals do not yield the octet spectrum and no free electrons are generated with this low-energy setup. Furthermore, a direct formation of **3** by UV damage of the thymine base can also be excluded, because no signal was observed by using thymine or thymidine instead of **1**. Finally, the possibility of an intermolecular ET between two molecules of **1** could be ruled out because of the weak signal intensity, which corresponds to a radical concentration below 1  $\mu$ molar, as well as the linear dependence of the signal intensity on concentration.

The assumption that the proton originates from a C,H-bond of the sugar is based on the fact that exchanging  $H_2O$  for  $D_2O$  does not change the octet spectrum, which excludes the solvent as the source of the proton. Additionally, the proton transfer has to be faster than the EPR timescale, because a doublet spectrum<sup>[15]</sup> of the thymine radical anion was not observed, which may imply that the hydrogen transfer is coupled with the electron transfer,

or that the reaction occurs directly by hydrogen-atom transfer. Also, the doublet of the thymine radical anion cannot be a constituent of the central part spectrum, because addition of the electron quencher did not lead to an intensity decrease for any two lines within the central part spectrum.

All these experiments, and the short distance of about 4 Å between the tertiary  $\beta$ -C,H-bond of the carbohydrate and the thymine, make a proton-coupled electron transfer (or hydrogen-atom transfer) between the 4'-deoxyribose and the thymine plausible.

It should be mentioned that irradiation of the nucleotide derivative of **1** incorporated into DNA oxidises guanine and does not reduce thymine bases, as shown earlier.<sup>[2f-j]</sup> This different reaction behaviour is based on the presence of different 3' groups, that is, hydroxy for the nucleoside **1** and phosphate for the nucleotide of **1** that is incorporated into DNA. Phosphate is an excellent leaving group, whose immediate heterolytic cleavage from the 3' site after the formation of the 4'-carbohydrate radical results in the formation of a sugar radical cation,<sup>[10]</sup> which is able to oxidise guanines but not to reduce thymines.<sup>[20]</sup> The nucleoside **1** alone, with the poor hydroxy leaving group in the 3'-position, does not form the cation radical but follows the reaction pathway **2**  $\rightarrow$  **3** to the thymyl radical. Schulte-Frohlinde and co-workers showed sometime ago that the 3'-OH group can be protonated and thereby be transformed to a good H<sub>2</sub>O leaving group at acidic pH values,<sup>[21]</sup> however, the experiments reported here were performed at pH 7 or in acetonitrile, which renders a 3'-OH protonation unlikely. To generate thymyl radicals in DNA site specifically, nucleoside **1** has to be attached to the DNA at the 3' end or by an ether linkage.

## Experimental Section

The thymidine derivative **1** was prepared as described previously.<sup>[22]</sup> Appropriate amounts of **1** were dissolved in dry acetonitrile (CH<sub>3</sub>CN) or in H<sub>2</sub>O or D<sub>2</sub>O, yielding final concentrations of 20 mM if not stated otherwise. The samples were deoxygenated, filled with argon, transferred into standard X-band EPR tubes (quartz, outer diameter 4 mm, internal diameter 2.4 mm) under argon and frozen in liquid nitrogen (77 K). The samples were photolyzed for 200 s at 77 K outside of the cavity, using a Hg-Arc lamp of 100 W in conjunction with a 320 nm cut-off filter. In the case of the measurements at 4 K, the sample irradiation was performed directly in the EPR cavity. Samples of thymine, thymidine and di-*t*-butylketone were prepared and treated in the same way. The electron scavenger K<sub>3</sub>[Fe(CN)<sub>6</sub>] was added in a concentration of 1 mM, according to Hüttermann and co-workers.<sup>[23]</sup>

EPR spectra were recorded on a Bruker ESP300E EPR spectrometer equipped with a TM<sub>102</sub> rectangular resonator and a cryostat from Oxford for measurements at 77 K and 4 K. Simulations and further data processing were performed with Simfonia and WinEPR from Bruker.

## Acknowledgements

The DFG is thanked for financial support and for a Habilitation fellowship to O.S. B.G. thanks the SNF for financial support. E.F. thanks the University of Padova for financial aid.

**Keywords:** DNA • electron transfer • EPR spectroscopy • nucleotides • radicals

- [1] a) N. J. Turro, J. K. Barton, *J. Biol. Inorg. Chem.* **1998**, *3*, 201; b) M. W. Grinstaff, *Angew. Chem.* **1999**, *111*, 3845; *Angew. Chem. Int. Ed.* **1999**, *36*, 2714; c) Y. A. Berlin, A. L. Burin, M. A. Ratner, *Superlattices Microstruct.* **2000**, *28*, 241.
- [2] a) S. Hess, M. Götz, W. B. Davis, M. E. Michel-Beyerle, *J. Am. Chem. Soc.* **2001**, *123*, 10046; b) M. Bixon, B. Giese, S. Wesseley, T. Langenbacher, M. E. Michel-Beyerle, J. Jortner, *Proc. Natl. Acad. Sci. USA* **1999**, *96*, 11713; c) F. D. Lewis, R. S. Kalgutkar, Y. Wu, X. Liu, J. Liu, R. T. Hayes, M. R. Wasielewski, *J. Am. Chem. Soc.* **2000**, *122*, 12346; d) F. D. Lewis, X. Liu, J. Liu, S. E. Miller, R. T. Hayes, M. R. Wasielewski, *Nature* **2000**, *406*, 51; e) C. Wan, T. Fiebig, O. Schiemann, J. K. Barton, A. H. Zewail, *Proc. Natl. Acad. Sci. USA* **2000**, *97*, 14052; f) B. Giese, J. Amaudrut, A. K. Köhler, M. Spormann, S. Wesseley, *Nature* **2001**, *412*, 318; g) T. Kendrick, B. Giese, *Chem. Commun.* **2002**, 2016; h) B. Giese, *Acc. Chem. Res.* **2000**, *33*, 631; i) E. Meggers, A. Dussy, T. Schäfer, B. Giese, *Chem. Eur. J.* **2000**, *6*, 485; j) A. Dussy, E. Meggers, B. Giese, *J. Am. Chem. Soc.* **1998**, *120*, 7399.
- [3] a) B. Giese, *Curr. Opin. Chem. Biol.* **2002**, *6*, 612; b) B. Giese, A. Bieland, *Chem. Commun.* **2002**, 667.
- [4] H. A. Wagenknecht, *Angew. Chem.* **2003**, *115*, 2558; *Angew. Chem. Int. Ed.* **2003**, *42*, 2454.
- [5] a) K. Hildenbrand, G. Behrens, D. Schulte-Frohlinde, J. N. Herak, *J. Chem. Soc. Perkin Trans.* **1989**, *2*, 283; b) S. Steenken, *Chem. Rev.* **1989**, *89*, 503; c) D. J. Deeble, M. N. Schuchmann, S. Steenken, C. von Sonntag, *J. Phys. Chem.* **1990**, *94*, 8186; d) B. Weiland, J. Hüttermann, *Int. J. Radiat. Biol.* **1998**, *74*, 341; e) A. Gräslund, A. Ehrenberg, A. Rupprecht, G. Ström, *Biochim. Biophys. Acta* **1971**, *254*, 172; f) P. M. Cullis, M. E. Malone, L. A. Merson-Davies, *J. Am. Chem. Soc.* **1996**, *118*, 2775; g) J. H. Miller, D. L. Frasco, C. E. Swanberg, A. Rupprecht in *Radiation Research: A Twentieth Century Perspective*, vol. 2 (Eds.: J. D. Chapman, W. C. Dewey, G. F. Witmore), Academic Press, San Diego, **1992**.
- [6] a) A. Messer, K. Carpenter, K. Forzley, J. Buchanan, S. Yang, Y. Razskazovskii, Z. Cai, M. D. Sevilla, *J. Phys. Chem. B* **2000**, *104*, 1128; b) Z. Cai, M. D. Sevilla, *J. Phys. Chem. B* **2000**, *104*, 6942; c) Z. Cai, X. Li, M. D. Sevilla, *J. Phys. Chem. B* **2002**, *106*, 2755.
- [7] a) A. Schwögler, L. T. Burgdorf, T. Carell, *Angew. Chem.* **2000**, *112*, 4082; *Angew. Chem. Int. Ed.* **2000**, *39*, 3918; b) C. Behrens, L. T. Burgdorf, A. Schwögler, T. Carell, *Angew. Chem.* **2002**, *114*, 1841; *Angew. Chem. Int. Ed.* **2002**, *41*, 1763.
- [8] a) N. Amann, E. Pandurski, T. Fiebig, H. A. Wagenknecht, *Angew. Chem.* **2002**, *114*, 3084; *Angew. Chem. Int. Ed.* **2002**, *41*, 2978; b) N. Amann, E. Pandurski, T. Fiebig, H. A. Wagenknecht, *Chem. Eur. J.* **2002**, *8*, 4877.
- [9] F. D. Lewis, X. Liu, S. E. Miller, R. T. Hayes, M. R. Wasielewski, *J. Am. Chem. Soc.* **2002**, *124*, 11280.
- [10] a) B. Giese, A. Dussy, C. Elie, P. Erdmann, U. Schwitter, *Angew. Chem.* **1994**, *106*, 1941; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1861; b) B. Giese, X. Beyrich-Graf, P. Erdmann, L. Giraud, P. Imwinkelried, S. N. Müller, U. Schwitter, *J. Am. Chem. Soc.* **1995**, *117*, 6146; c) S. Peukert, R. Batra, B. Giese, *Tetrahedron Lett.* **1997**, *38*, 3507; d) A. Guggler, R. Batra, P. Rzadek, G. Rist, B. Giese, *J. Am. Chem. Soc.* **1997**, *119*, 8740.
- [11] N. J. Turro *Modern Molecular Photochemistry*, University Science Books, Sausalito, **1991**.
- [12] J. Dupuis, B. Giese, D. Rügge, H. Fischer, H.-G. Korth, R. Sustmann, *Angew. Chem.* **1984**, *96*, 887; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 896.
- [13] P. B. Ayscough, C. Thomson, *Trans. Faraday Soc.* **1962**, *58*, 1477.
- [14] J. Hüttermann, M. Röhrig, W. Köhnlein, *Int. J. Radiat. Biol.* **1992**, *61*, 299.
- [15] P. M. Cullis, J. D. McClymont, M. E. Malone, A. M. Mather, I. D. Podmore, M. C. Sweeny, M. C. R. Symons, *J. Chem. Soc. Perkin Trans. 2* **1992**, 1695.
- [16] a) S. Gregoli, M. Olast, A. Bertinchamps, *Radiation Res.* **1976**, *65*, 202; b) B. Pruden, W. Snipes, W. Gordy, *Proc. Natl. Acad. Sci. USA* **1965**, *53*, 917.
- [17] H. Schuh, E. J. Hamilton, H. Paul, H. Fischer, *Helv. Chim. Acta* **1974**, *57*, 2011.
- [18] The HPLC profile (Supporting Information) of the irradiated sample showed a small peak appearing at a retention time characteristic for a deoxyribose derivative after the photocleavage of the pivaloyl group. An analysis of this signal by mass spectroscopy was not possible due to the low conversion of the reactant.

- [19] J. Hüttermann, W. A. Bernhard, E. Haindl, G. Schmidt, *J. Phys. Chem.* **1977**, *81*, 228.
- [20] The same kind of EPR study was done on a double-stranded DNA in which a thymine nucleotide in the middle of the sequence was modified at the 4' sugar site with a pivaloyl group. No appearance of the eight-line spectrum, also characteristic for a thymyl radical in DNA,<sup>[5d]</sup> could be detected. The spectrum (Supporting Information) shows a different pattern and is still under analysis.
- [21] a) C. von Sonntag, U. Hagen, A.-M. Schön-Bopp, D. Schulte-Frohlinde, *Adv. Radiat. Biol.* **1981**, *9*, 109; b) C. von Sonntag, *The Chemical Basis of Radiation Biology*, Taylor & Francis, London, **1987**; c) G. Behrens, G. Klotzenburg, D. Schulte-Frohlinde, *Z. Naturforsch C* **1982**, *37*, 1205.
- [22] A. Marx, P. Erdmann, M. Senn, S. Körner, T. Jungo, M. Petretta, P. Imwinkelried, A. Dussy, K. J. Kulicke, L. Macko, M. Zehnder, B. Giese, *Helv. Chim. Acta* **1996**, *79*, 1980.
- [23] M. Lange, B. Weiland, J. Hüttermann, *Int. J. Radiat. Biol.* **1995**, *68*, 475.

Received: June 30, 2003 [Z 896]

Revised: October 15, 2003

## Electrochemical Doping of Double-Walled Carbon Nanotubes: An In Situ Raman Spectroelectrochemical Study

Ladislav Kavan,<sup>\*[a]</sup> Martin Kalbáč,<sup>[a, b]</sup>  
Markéta Zukalová,<sup>[a]</sup> Matthias Krause,<sup>[b]</sup> and  
Lothar Dunsch<sup>[b]</sup>

Double-walled carbon nanotubes (DWCNTs) occupy a unique position between the single-walled (SWCNTs) and multiwall carbon nanotubes, which predestinates the DWCNT for fundamental experimental and theoretical studies. The DWCNTs can be prepared by catalytic arc discharge<sup>[1, 2]</sup> or by pyrolysis of fullerene peapods C<sub>60</sub>@SWCNT.<sup>[3, 4]</sup> The diameters of DWCNT grown in arc discharge conditions in an H<sub>2</sub> atmosphere were 3.5–6.5 nm.<sup>[1]</sup> Recently, Shinohara and co-workers<sup>[2]</sup> have prepared high-quality DWCNTs in pulsed arc discharge. These tubes exhibited the inner and outer diameters of 0.8–1.2 nm and 1.6–2.0 nm, respectively.<sup>[2]</sup> The DWCNTs made by pyrolysis of peapods were considerably narrower than the arc-grown DWCNTs. The diameters of ex-peapod DWCNTs were roughly the same as the diameters of the parent structures, that is, C<sub>60</sub> and SWCNT. As the optimum diameter of SWCNT for peapod filling is between 1.3–1.4 nm, the ex-peapod DWCNT exhibited

the diameters of inner and outer tubes of 0.6–0.9 nm and 1.3–1.4 nm, respectively.<sup>[1, 3, 5]</sup>

The Raman scattering in DWCNT is resonant and diameter-selective in terms of the allowed optical transitions between van Hove singularities (vHs). The diameter dependence of the radial breathing mode (RBM) allows easy distinction of inner and outer tubes.<sup>[2–5]</sup> In contrast to the arc-grown DWCNTs, the ex-peapod DWCNTs exhibited unusually sharp Raman lines of the RBM of the inner tubes.<sup>[2–5]</sup> This result demonstrates higher structural perfection of the inner tubes, provided they grow from fullerenes by “epitaxial deposition” on the inner wall of the outer tube.<sup>[5]</sup> Kuzmany and co-workers<sup>[5]</sup> have recently assigned all the RBMs of semiconducting inner tubes to the particular chiral indexes (*n*, *m*).

In situ Raman spectroelectrochemistry allows monitoring of charge-transfer modifications of resonance Raman scattering in SWCNTs,<sup>[6–8]</sup> C<sub>60</sub>@SWCNT (peapods<sup>[9]</sup>), and C<sub>70</sub>@SWCNT (peapods<sup>[9]</sup>). The electrochemical charging of intratubular fullerene in peapods was sluggish, hence, the double-layer charging primarily influenced the wall of the peapods.<sup>[9]</sup> However, this caused various peculiarities, such as the “anodic enhancement” of Raman intensities of intratubular fullerene, which was specific only for the C<sub>60</sub> but not for the C<sub>70</sub> encapsulated in SWCNT.<sup>[9]</sup>

To our knowledge, there is no similar electrochemical and spectroelectrochemical study of DWCNT. This raises a motivation to fill the gap and to explore the expected distinction in electrochemical charging of the inner and outer tubes of DWCNT.

Figure 1 shows the Raman spectra (excited at 2.41 eV) in the range of tangential displacement mode (TM) of DWCNTs compared with the spectra of the parent materials of the “first and second generation”, that is, SWCNT and C<sub>60</sub>@SWCNT, respectively. (For spectroelectrochemical details on the parent materials, see ref. [9]). The green laser (2.41 eV) resonates with the second transition between vHs in semiconducting inner tubes (v<sub>2</sub><sup>2</sup> → c<sub>2</sub><sup>2</sup>) and with the third transition between vHs in semiconducting outer tubes (v<sub>3</sub><sup>3</sup> → c<sub>3</sub><sup>3</sup>).<sup>[4]</sup> Eklund and co-workers<sup>[4]</sup> have fitted the TM band of pristine SWCNT, C<sub>60</sub>@SWCNT, and DWCNT to three to four Lorentzian components, but there was no significant difference in the line positions and shape of the TM spectra between these three materials at the 2.41-eV excitation. However, with the red laser (1.83 eV) there was a new band at 1587 cm<sup>-1</sup>, specific for DWCNTs only. This band appeared in addition to the main line at 1590 cm<sup>-1</sup>, the latter was assigned to the outer tube.<sup>[4]</sup>

Electrochemical doping of nanotubes<sup>[7, 8]</sup> and peapods<sup>[9]</sup> causes mostly capacitive double-layer charging with small contributions, if any, of Faradaic pseudocapacitance of surface oxides assumed on defect tubes. The same electrochemical behavior was also traced for our DWCNT samples (data not shown). The TM band of SWCNT exhibits the expected drop of intensity and blue shift upon positive charging (Figure 1). These effects are due to quenching of optical transitions between vHs and stiffening of the graphene mode if holes are introduced into the π band.<sup>[7, 8]</sup> Also we may note the previously reported<sup>[9]</sup> “anodic enhancement” of the pentagonal pinch mode, A<sub>g</sub>(2), of the intratubular fullerene in C<sub>60</sub>@SWCNT. The absence of A<sub>g</sub>(2)

[a] Prof. Dr. L. Kavan, Dr. M. Kalbáč, Dr. M. Zukalová  
J. Heyrovský Institute of Physical Chemistry  
Academy of Sciences of the Czech Republic  
Dolejškova 3, CZ-182 23 Prague 8 (Czech Republic)  
Fax: (+420) 2-8658-2307  
E-mail: kavan@jh-inst.cas.cz

[b] Dr. M. Kalbáč, Dr. M. Krause, Prof. Dr. L. Dunsch  
Institute of Solid State and Materials Research  
Helmholtzstraße 20, 01069 Dresden (Germany)