SUPPORTING INFORMATION

Tautomerism in Guanyl Radical

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Rate constants for the reactions of hydrated electrons with substrates. The pseudo first-order rate constant, k_{obs}, for the reaction of e_{aq}^- with a variety of substituted guanine derivatives were determined by measuring the rate of the optical density decrease of e_{aq}^- at 720 nm (ε = 1.9×10^4 M^{-1}cm^{-1}) at pH ≈7.[1] From the slope of k_{obs} vs. nucleoside concentration, the bimolecular rate constants (k) were determined. Figures S1 and S2 show the case of unsubstituted guanosine (**1a**) and 2'-deoxyguanosine (**1b**), respectively, whereas Figures S3 and S4 show the experiments with 8-chloroguanosine (**8**) and 8-iodoguanosine (**9**), respectively.

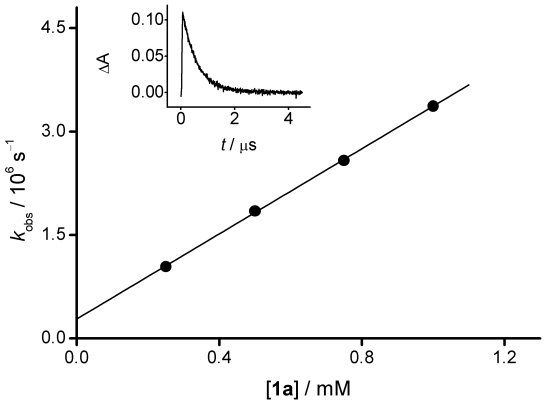

Figure S1. Plot of k_{obs} vs [**1a**] for the decay of e_{aq}^- at 720 nm from the pulse radiolysis of Ar-purged solutions containing 0.25 M *t*-BuOH at pH ≈7: Inset: Decay of e_{aq}^- in the presence of 0.5 mM **1a**; optical path = 2.0 cm, dose = 10.0 Gy. The solid line represents the first-order kinetic fit to the data.

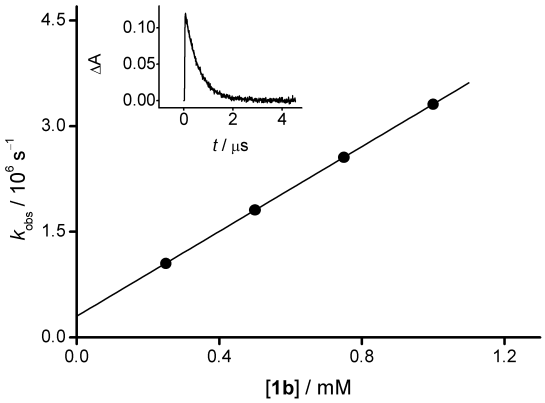

Figure S2. Plot of k_{obs} vs [**1b**] for the decay of e_{aq}^- at 720 nm from the pulse radiolysis of Ar-purged solutions containing 0.25 M *t*-BuOH at pH ~7: Inset: Decay of e_{aq}^- in the presence of 0.5 mM **1b**; optical path = 2.0 cm, dose = 11.0 Gy. The solid line represents the first-order kinetic fit to the data.

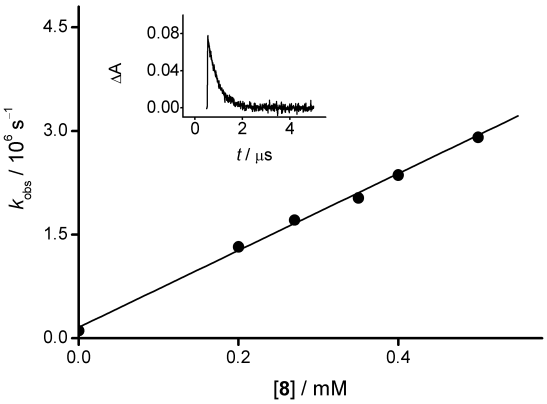

Figure S3. Plot of k_{obs} vs [**8**] for the decay of e_{aq}^- at 720 nm from the pulse radiolysis of Ar-purged solutions containing 0.25 M *t*-BuOH at pH ~7: Inset: Decay of e_{aq}^- in the presence of 0.4 mM **8**; optical path = 2.0 cm, dose = 6.9 Gy. The solid line represents the first-order kinetic fit to the data.

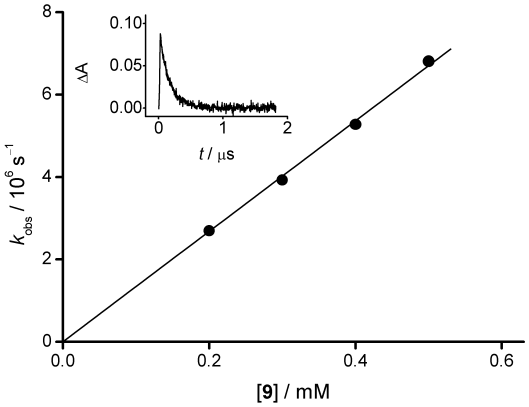

Figure S4. Plot of k_{obs} vs [**9**] for the decay of e_{aq}^- at 720 nm from the pulse radiolysis of Ar-purged solutions containing 0.25 M *t*-BuOH at pH 7: Inset: Decay of e_{aq}^- in the presence of 0.5 mM **9**; optical path = 2.0 cm, dose = 7.5 Gy. The solid line represents the first-order kinetic fit to the data.

8-Bromo-2'-deoxyguanosine (13). Ar-purged aqueous solutions of 8-bromo-2'-deoxyguanosine (1 mM) and *t*-BuOH (0.25 M) at pH 7 were prepared. The spectral changes obtained from the pulse irradiation of a solution containing **13** are shown in Figure S5. The optical absorption spectrum taken 2 μs after the pulse (solid circles) originated from the reaction of **13** with e_{aq}^-. The disappearance of this species gave rise to a new transient species whose spectrum was taken 40 μs after the pulse (open triangles). By monitoring the reaction at 600 nm and analyzing the trace (Inset of Figure S5) using the treatment for consecutive reactions, a first-order rate constant of 1×10^5 s^{-1} was obtained for the faster process relevant to the present study.The last transient is very similar to that obtained after the oxidation of **1b** by $SO_4^{\bullet-}$ at pH 7, i.e., radical **3** (Scheme 1).[2]

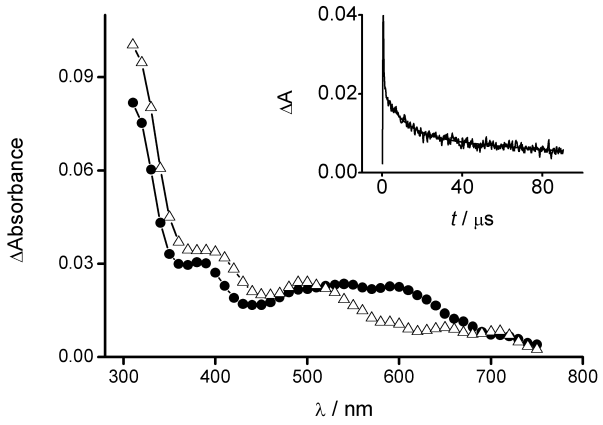

Figure S5. Absorption spectra obtained from the pulse radiolysis of Ar-purged solutions containing 1 mM **13** and 0.25 M *t*-BuOH at pH 7, taken 2 (●) and 40 μs (Δ) after the pulse; optical path = 2.0 cm, dose per pulse = 26.2 Gy. Inset: Time dependence of absorption at 600 nm. The initial fast decay is due to the disappearance of e_{aq}^-. The solid line represents the fit to the data obtained using the treatment for consecutive reactions (see text).

The reaction of e_{aq}^- with **13** was also studied at pH 13. The optical absorption spectrum, taken 5 μs after the pulse, is shown in Figure S6 (open circles). Now, the spectrum resembled in shape and λ-values that of radical **4**. In order to closely compare the two spectra, we also examined the reactions of $Br_2^{\bullet-}$ with **1b**.[3] The optical absorption spectra obtained at pH 13 after the completion of the reaction between **1b** and $Br_2^{\bullet-}$ (15 μs after the pulse) are also shown in Figure S6 (solid triangles). As can be seen, the two spectra are identical.[2] The bimolecular rate constant for the reaction of e_{aq}^- with **13** is found to be $(4.5\pm0.1)\times10^9$ M^{-1} s^{-1} at pH 13 (Inset of Figure S6).

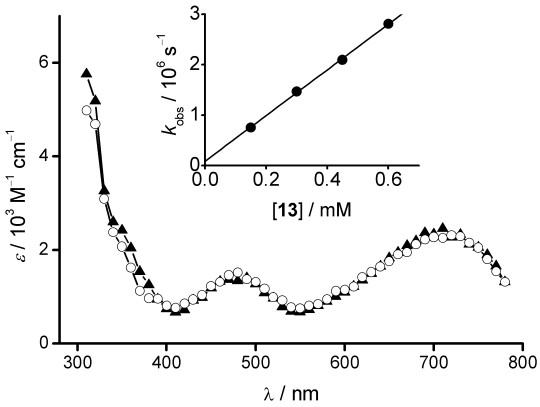

Figure S6. Absorption spectra obtained from the pulse radiolysis of solutions at pH 13 of: (❍) 1 mM **13** and 0.25 M *t*-BuOH, Ar-purged, taken 5 μs after the pulse; (▲) 1 mM **1b** and 0.1 M KBr, N_2O-saturated, taken 15 μs after the pulse. Inset: Plot of k_{obs} vs [**13**] for the decay of e_{aq}^- at 720 nm from the pulse radiolysis of Ar-purged solutions containing 0.25 M *t*-BuOH and 0.1 M NaOH; dose per pulse = 7.7 Gy.

Continuous Radiolysis and Product Analysis. Figure S7 shows four examples of 8-bromoguanine derivatives carried out in a similar manner as those described for **6**.[4] Deareated aqueous solutions containing **13**, **15**, **16** or **17** (ca. 1.5 mM) and *t*-BuOH (0.25 M) at pH ~7 were irradiated under stationary-state conditions with a dose rate of ca. 15 Gy/min followed by HPLC analysis. The solution at pH ~7 (i.e., natural without additives) before and after the irradiation dose of 2 kGy gave pH 7.6 and 5.7, respectively. The debrominated compounds (**1b**, **20**, **21** or **22**, respectively) were the only detectable products and mass balances were close to 100%. Analysis of the data in terms of radiation chemical yield (G),[5] gives G(–**13**)=0.34, G(**1b**)=0.31, G(–**15**)=0.36, G(**20**)=0.31, G(–**16**)=G(**21**)=0.33, and G(–**17**)=0.34, G(**22**)=0.30 μmol J^{-1}.

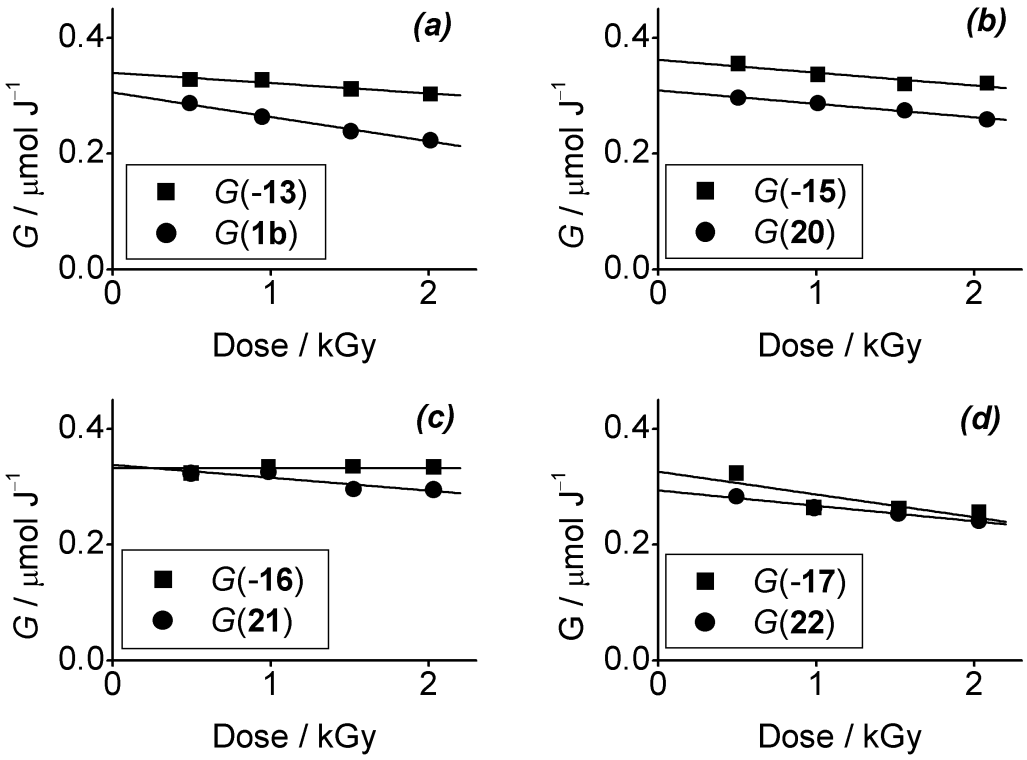

Figure S7. Radiation chemical yields (*G*) as a function of irradiation dose for the consumption of **13**, **15**, **16** or **17** and the formation of **1b**, **20**, **21** or **22**, respectively, obtained from the continuous radiolysis of vacuum degassed solutions containing ca. 1.5 mM substrate and 0.25 M *t*-BuOH at pH ≈7. The lines are the linear fit to the data.

Computational details. Hybrid meta DFT calculations with the B1B95 (Becke88[6]-Becke95[7] 1-parameter model for thermochemistry) functional[8] were carried out using the Gaussian 03 system of programs.[9] Note that the percentage of HF exchange is 28% whereas in reference 9 is incorrectly coded as 25%.

DFT Calculations

Table S1. Relative B1B95/6-31+G** energy ΔE and TD-B3LYP/6-311G**//B1B95/6-31+G** optical transitions for the 8-bromo-9-methylguanine radical anion (**26**) protonated at different atoms

Protonated atom	ΔE/kJ mol^{-1}	λ/nm	f
N7	0.0	306	0.015
		362	0.107
		423	0.037
C2	30.1	299	0.145
		323	0.017
		416	0.037
C4	49.8	304	0.44
		329	0.068
		355	0.027
		381	0.040
C5	67.0	311	0.069
		343	0.011
		442	0.016
		501	0.035
N3	84.5	291	0.017
		304	0.029
		315	0.084
		354	0.013
O	107.1	277	0.074
		340	0.040
		452	0.028
C8[a]	–42.0	-	-

[a]The radical tends to lose Br forming in the gas phase a π-complex (see Figure 7).

Table S2. TD-B3LYP/6-311G**//B1B95/6-31+G** optical transitions for the various tautomeric forms of one-electron oxidized 9-methylguanine.

radical	□/nm	f
27	283	0.066
	348	0.058
	466	0.014
28	284	0.050
	347	0.044
	421	0.011
	606	0.052
29	280	0.015
	360	0.068
	423	0.014
	1151	0.023
30	302	0.078
	308	0.019
	411	0.038
	484	0.045

References and Notes

(1) Hug, G. L. *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.* **1981**, *69*, 6.

(2) It is worth mentioning that the decays of transients **3** or **4** did not give rise to absorbing species at □ > 320 nm.

(3) The reactions were carried out in N_2O-saturated solutions containing 0.1 M KBr. See: Jovanovic, S.V.; Simic, M.G. *J. Phys. Chem.* **1986**, *90*, 974.

(4) Ioele, M.; Bazzanini, R.; Chatgilialoglu, C.; Mulazzani, Q.G. *J. Am. Chem. Soc.* **2000**, *122*, 1900.

(5) The disappearance of the starting material or the appearance of the product (mol/kg) divided by the absorbed dose (1 Gy = 1 J/kg) gives the radiation chemical yield (*G*).

(6) Becke, A.D. *Phys. Rev. A* **1988**, *38*, 3098.

(7) Becke, A.D. *J. Chem. Phys.* **1996**, *104*, 1040-1046.

(8) Zhao, Y.; Pu, J.; Lynch, B.J.; Truhlar, D.G. *Phys. Chem. Chem. Phys.* **2004**, *6*, 673.

(9) Gaussian 03, Revision B.5, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh PA, 2003.