Polymerization Initiation by *N*-*p*-Tolylglycine: Free-Radical Reactions Studied by Pulse and Steady-State Radiolysis

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SYNOPSIS

The extensive use of *N*-*p*-tolylglycine (NTG) and analogous compounds in adhesive bonding technologies requires a better understanding of their role in initiating free-radical polymerization. The fast oxidation and reduction reactions of NTG proceed via the formation of various free radicals and radical cation and anion intermediates. These intermediates were identified and their reactivity with oxygen, to produce the corresponding peroxyl radicals, was measured. Hydroxyl radicals (ȮH) were used to initiate oxidation reactions of NTG, while the reduction reactions were initiated with hydrated electrons (e^-_{aq}). OH radicals react with NTG predominately by addition to the aromatic ring followed by OH^- elimination to produce $NTG^{+\cdot}$ radical cations. In the presence of oxygen, the OH-NTG$^\cdot$ adduct also reacts with oxygen to produce peroxyl radicals. The reaction of NTG with e^-_{aq} forms the radical anion, which subsequently protonates on the aromatic ring to produce cyclohexadienyl radicals, or undergoes an amine elimination to yield an acetic acid free radical and 4-methylaniline. Hydroperoxyl radicals ($HO^\cdot_2$) abstract hydrogen from the α position of NTG to form the corresponding alkyl free radical. © 1994 John Wiley & Sons, Inc.[†]

INTRODUCTION

For achieving adhesive bonding between dental methacrylate resins and hard tooth tissues, NPG-GMA (the addition reaction product of *N*-phenylglycine and glycidyl methacrylate) was synthesized and studied.[1-3] The rationale was based on providing a compound that could make water-resistant attachments to tooth surfaces and also copolymerize with MA resins or composites. This adhesion mechanism was patterned after: organofunctional silane coupling agents that effectively improve bonding between resins and glass surfaces[4]; mordants and mordant dye attachments in textile and protein colorations[5,6]; the teachings of Zisman[7] and his associates relating to physical/chemical surface interactions; and other considerations.

However, on further investigation of NPG-GMA and NTG-GMA (the adduct of *N*-*p*-tolylglycine and glycidyl methacrylate) and other related compounds such as NTG, it gradually became apparent that such compounds may perform another function: they produce free radicals that initiate the polymerization of adhesive bonding resins. The dissolution of such compounds in MA monomers usually results in gelation or polymerization of such formulations. The apparent production of free radicals by NTG-GMA and related compounds has both positive and negative ramifications: the usefulness and effectiveness in clinical adhesive bonding formulations are probably improved, but storage stability is a problem. Although these compositions have been used principally for dental applications, there is potential for wider use in many industrial technologies. It is important to understand the mechanisms behind the "spontaneous" reactivity of

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these *N*-aryl-α amino acids in order to maximize both storage stability and adhesive bonding efficacy.

There are at least two current hypotheses relating to the production of free radicals by such compounds: an acid–amine interaction that has recently been described by Antonucci et al.[8] and an autoxidative sequence of events involving the methylene group in the molecule.[9] The former might be a source of free radicals through carboxylic acid–amine complexation and subsequent decomposition of the complex and the latter might lead to the production of hydroxyl and peroxyl radicals formed with oxygen in a branching chain reaction. Indirect evidence is emerging that hydroxyl radicals may be involved in autoxidative decompositions of these amino acids during storage. It is the purpose of the present study to investigate the characteristics of free radicals derived from NTG, a simple member of this class of compounds. This knowledge may help elucidate the mechanisms of polymerization-inducing reactions[10] of *N*-aryl-α amino acids as well as the mechanisms of their discoloration and decomposition in an oxidizing environment,[11] for example during storage of their solutions in air.

EXPERIMENTAL

Radiolysis of water generates in the first step ȮH (2.9×10^{-7} mol J^{-1}), hydrated electrons, e^-_{aq} (2.9×10^{-7} mol J^{-1}), and H atoms (0.6×10^{-7} mol J^{-1}), where the numbers in parenthesis indicate their radiation yields, *G*.

$$H_2O \xrightarrow{\text{ionizing radiation}} \dot{O}H + \dot{H} + e^-_{aq} + H_2 + H_2O_2 + H_3O^+.$$

For radiolytic oxidation of NTG, aqueous solutions were saturated with N_2O to convert e^-_{aq} into ȮH radicals.[12] For reduction of NTG by hydrated electrons *t*-butanol was used to scavenge ȮH radicals and the solutions were deoxygenated by purging with pure dry N_2 for about 30 min.

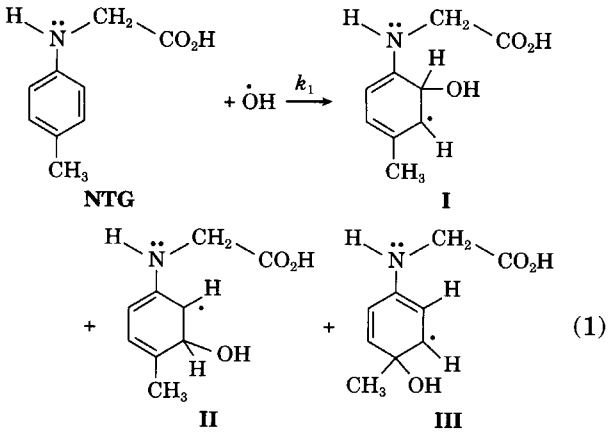
The kinetics and the spectra of the radicals were measured by pulse radiolysis techniques using a Febetron Model 705 field-emission accelerator (2-MeV electrons), supplying an absorbed dose adjustable from 2 to 200 Gy/50 ns pulse. The system for data acquisition and for kinetics and spectral measurements has been previously described.[13] Dosimetry for pulse radiolysis was performed in the same sample cells with the use of N_2O-saturated 0.01 mol L^{-1} KSCN solutions; the yield of $[(SCN)^-_2]$ was assumed to be 0.61 μmol J^{-1} and the molar extinction coefficient, ϵ_m, at 480 nm equal to 7600 L mol^{-1} cm^{-1}.

γ Irradiation was carried out in a γ cell-220 ^{60}Co source with a dose rate of 1.2 Gy min^{-1}. In the study of NTG reactivity with hydroperoxy radicals ($HO^\cdot_2$), a standard Clark electrode (ORION), fitted in an airtight irradiation vessel, was used to measure oxygen concentration changes before, during, and after γ irradiation.[14]

RESULTS AND DISCUSSION

Oxidation of NTG with ȮH Radicals

ȮH radicals were formed in N_2O-saturated solutions with a yield of $G = 5.8 \times 10^{-7}$ mol J^{-1}. ȮH radicals may add to the aromatic ring and abstract hydrogen atoms from —N—H and —CH_2— groups of NTG. The abstraction generally is less rapid than the addition, which may occur at various ring positions, with highest probability at the positions *ortho* and *para* to the amino group.[15–17]



(1)

The reaction rate constant of ȮH radicals with NTG was measured by following the build-up at 310 nm (maximum absorption of OH–NTG$^\cdot$ adducts). Figure 1 shows the pseudo first order rate constant as a function of NTG concentration with an absolute rate constant, k_1, of 1×10^{10} L mol^{-1} s^{-1}. This value was expected,[12] since the reaction rate constant of ȮH radicals with benzene and with aniline is 1×10^{10} L mol^{-1} s^{-1}.

The insert in Figure 1 demonstrates a typical kinetic trace obtained with pulse-irradiated N_2O-saturated NTG aqueous solutions at 460 nm, showing a fast step (2 μs) followed by a much slower step (40 μs). The transient absorption spectrum at the end of the fast step (Fig. 2) has two bands with maxima at 310 and 460 nm. The absorption maximum at 310 nm is typical of OH adducts to aromatic

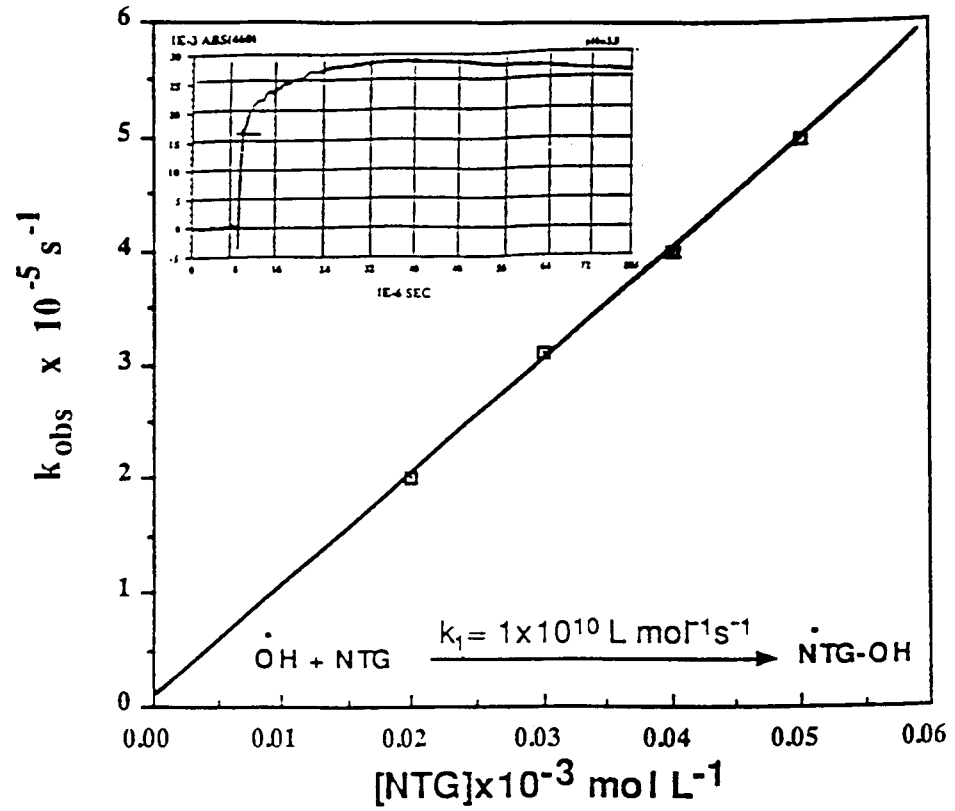


Figure 1 The increase in pseudo first-order rate constant for the buildup of OH–NTG• free radicals, at 310 nm, as a function of the NTG concentration in the pulsed N_2O-saturated solution. Dose = 4.7 Gy/pulse, pH = 3.9. Insert: A typical transient of the pulsed N_2O-saturated NTG aqueous solution at 460 nm. The fast component represents formation of NTG–$\dot{O}$H, while the slow component represents OH^- elimination. Dose = 4.7 Gy during the 50-ns pulse, pH = 3.9.

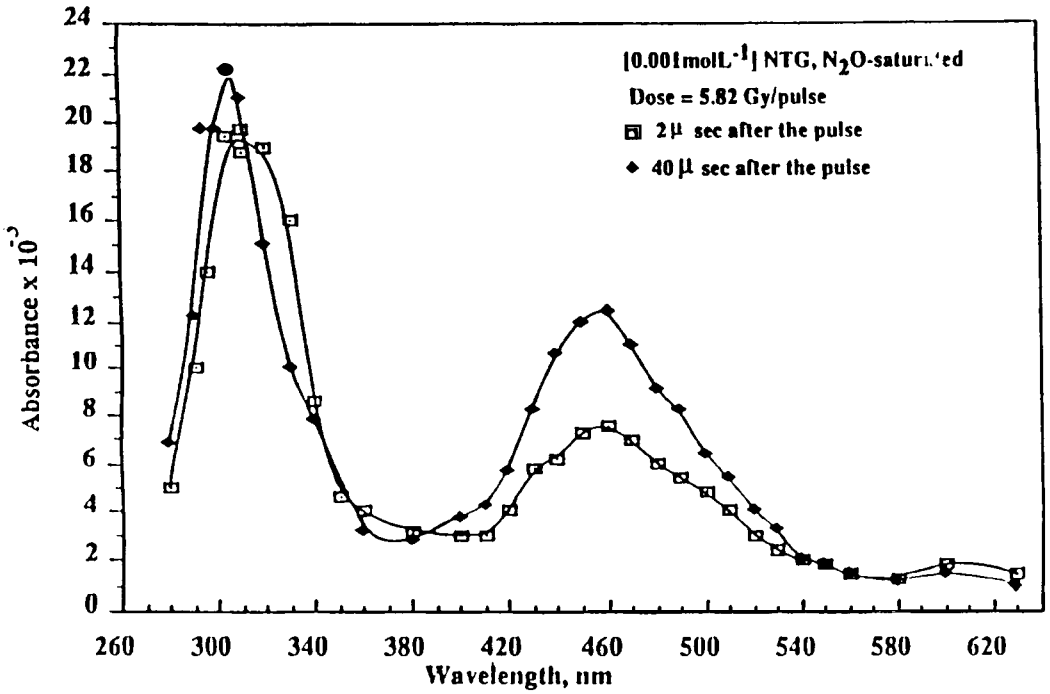
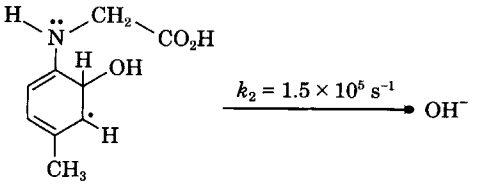


Figure 2 The transient absorption spectra, (□) at the end of the fast component (~ 2 μs after the pulse) and (♦) at the end of the slow component (~ 40 μs after the pulse), in the pulsed 0.001 mol L^{-1} NTG N_2O-saturated solutions. Dose = 5.8 Gy/pulse, pH = 3.9.

rings.[17] The maximum at 460 nm, however, is not typical of such adducts and suggests the formation of radical cations. The transient absorption spectrum (Fig. 2) at the end of the slower step, also has two absorption maxima at 305–310 and 460 nm. The peak at 460 nm can be ascribed to radical cations of NTG based on its similarity to the peak of radical cations obtained from aniline[18] (which was also confirmed by Raman and ESR studies).[19,20] The slow formation process is also similar to that observed with aniline and is interpreted as the elimination of OH^- from the OH adduct of the ring[18] (reaction 2). Because the amine group is electron donating, this elimination is fast for the *ortho* and *para* adducts but slow for the *meta* adduct.



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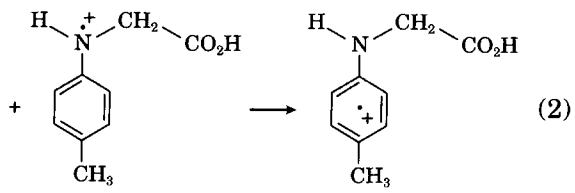
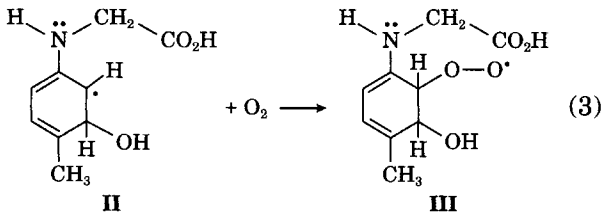


(2)

The finding that considerable absorption at 460 nm is formed during the fast process (2 μs after the pulse) suggests an additional route to formation of these radical cations. Possibly, some OH radicals add onto the nitrogen and undergo very rapid elimination of OH^- to result in fast oxidation of NTG to the radical cation.

The slow step of the OH^--elimination reaction was measured and found to have a rate constant of $k_{obs} = 1.5 \times 10^5\ s^{-1}$ at pH = 3.9. No dose–rate effect within the range of 3–30 Gy/pulse was detected; this indicates that the reaction was not a radical–radical reaction.

In the presence of O_2, the 310-nm peak was replaced by a 280-nm peak, but the 460-nm peak remained unchanged (Fig. 3). The latter peak was ascribed to NTG radical cations that are not expected to react with O_2. The 310-nm peak is probably due mostly to ring OH— adducts and thus disappears in the presence of O_2. Insert (a) in Figure 3 demonstrates the decay at 310 nm of the OH–NTG with oxygen via reaction 3; insert (b) represents the buildup at 460 nm (the formation of radical cations as a result of reaction 2). The rate constant for the decay at 310 nm was linearly dependent on O_2 concentration (Fig. 4), and a second-order rate constant of 1.4×10^9 L mol^{-1} s^{-1} was derived for reaction 3.



II III (3)

The peroxyl radical produced in reaction 3 exhibits a peak at 280 nm, similar to those reported previously for peroxyl radicals of this type.[17] Figure 5 shows the transient spectrum taken 2 ms after the pulse, by which time the 280 and 460 nm transient spectral decays were complete. The disappearance of the peak at 460 nm may be ascribed, at least in part, to a bimolecular reaction between the radical cations.[18] In addition, the resulting intermediates from the decay of OH–NTG–$O_2^{\cdot}$ peroxyl radicals (**III**) can also contribute to this spectrum.

Reaction of NTG with e_{aq}^- and H Atoms

Aromatic compounds such as benzene react with solvated electrons with rate constants of $\sim 10^7$ L mol^{-1} s^{-1}. The resulting radical anions are often very unstable and rapidly react with water to produce aromatic radicals equivalent to H adducts.[21]

The presence of a protonated amino group $-NH_2^+$, as would be formed in aqueous solutions of NTG at low pH conditions,[22] increases the reactivity toward e_{aq}^- as compared to the unprotonated —NH group. The reactions of e_{aq}^- with protonated β-phenylalanine, α-phenylglycine, and related compounds have been extensively studied.[17,23] It has been generally accepted that the e_{aq}^- reacts at the aliphatic group of such compounds, causing the elimination of ammonia or amines, or adds to the aromatic ring, with subsequent protonation to yield cyclohexadienyl radicals.[23]

Pulse radiolysis of deoxygenated solutions of NTG (0.001 mol L^{-1}) containing *t*-BuOH (1.2 mol L^{-1}) at pH 3.9 gave a transient spectrum with three peaks at about 330, 370, and 460 nm (Fig. 6). The rate of formation of the 330-nm peak was measured as a function of [NTG], and the second-order rate constant was found to be 2×10^9 L M^{-1} s^{-1}. This value agrees fairly well with the value at acidic pH.[23] It should be mentioned that e_{aq}^- reacts extremely fast with H_3O^+ at a reaction rate constant of 2.2×10^{10} L M^{-1} s^{-1}. From these values of rate constants for e_{aq}^- reactions with NTG and with H_3O^+, it is clear that under the conditions of Figure 6,

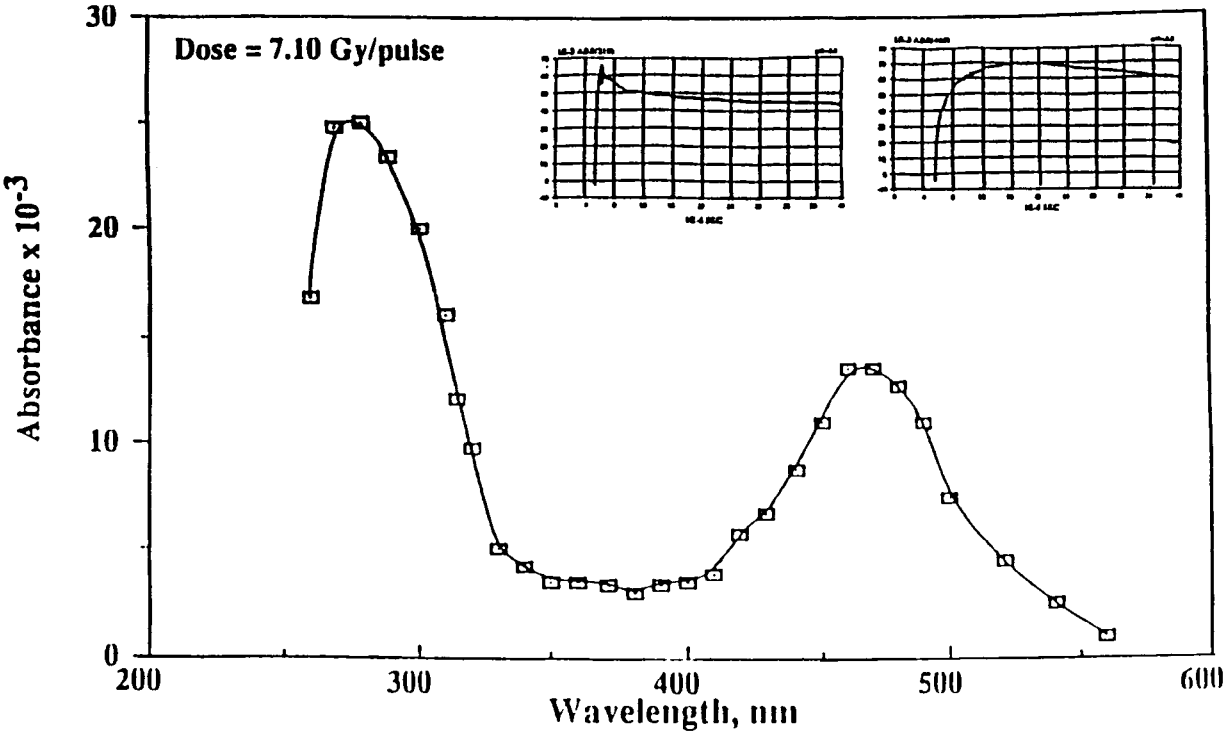


Figure 3 The transient absorption spectrum of OH–NTG–$O_2^{\cdot}$ peroxy radicals and the radical cations, 20 μs after the pulse solutions of 0.001 mol L^{-1} NTG saturated with 50% N_2O + 50% O_2 ($[O_2] = 0.6 \times 10^{-3}$ mol L^{-1}). Dose = 7.1 Gy, pH = 3.9. (a) The decay at (310) of OH–NTG$^{\cdot}$ (**II**) by its reaction with oxygen as in reaction scheme (3). (b) The formation of radical cations as shown by the buildup at 460 nm. Pulsed solution of N_2O/O_2-saturated solutions of 0.001 mol L^{-1} NTG. Dose = 7.0 Gy, pH = 3.9.

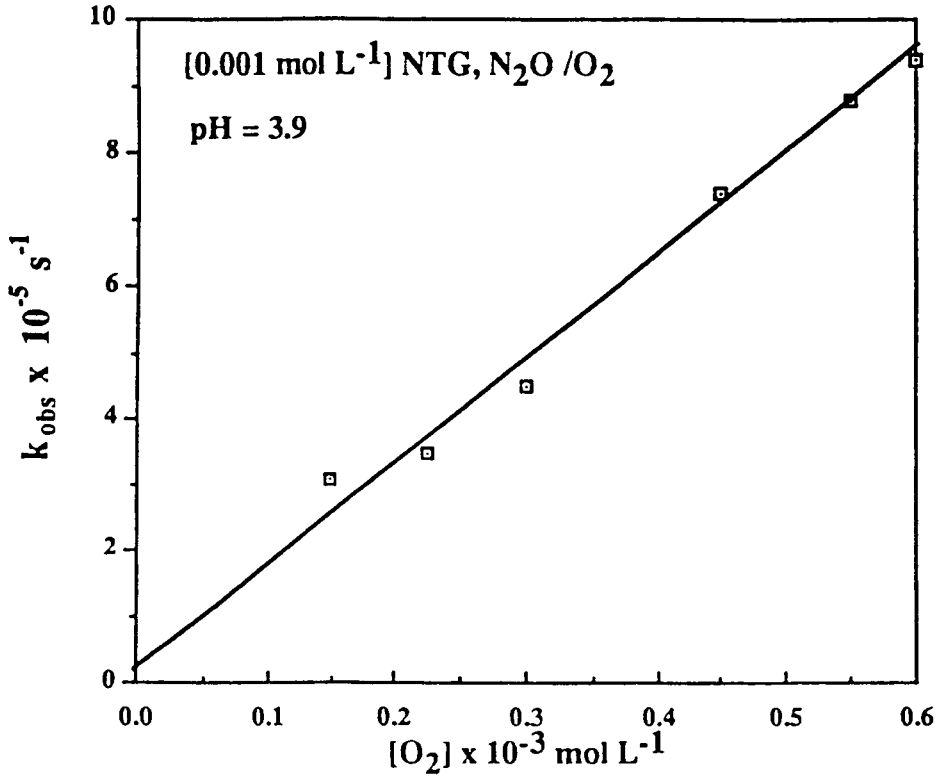


Figure 4 The increase in pseudo first-order rate constant for the decay of OH–NTG$^{\cdot}$ at 310 nm as a function of the $[O_2]$ concentration in the pulsed solution that was saturated with N_2O and O_2 and contained 0.001 mol L^{-1} of NTG. Dose = 4.5 Gy/pulse, pH = 3.9.

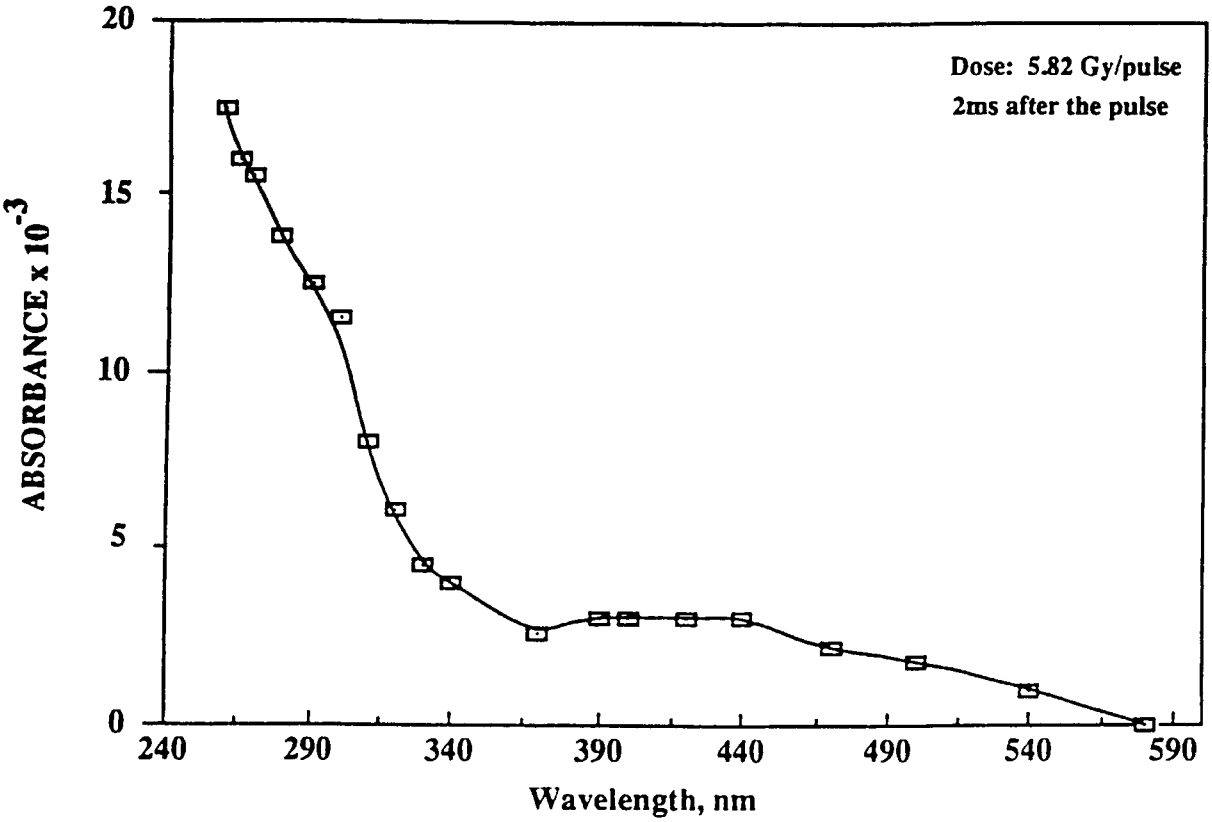


Figure 5 The transient absorption spectrum (2 ms after the pulse) of solutions of 0.001 mol L^{-1} NTG saturated with 50% N_2O + 50% O_2, pH = 3.9.

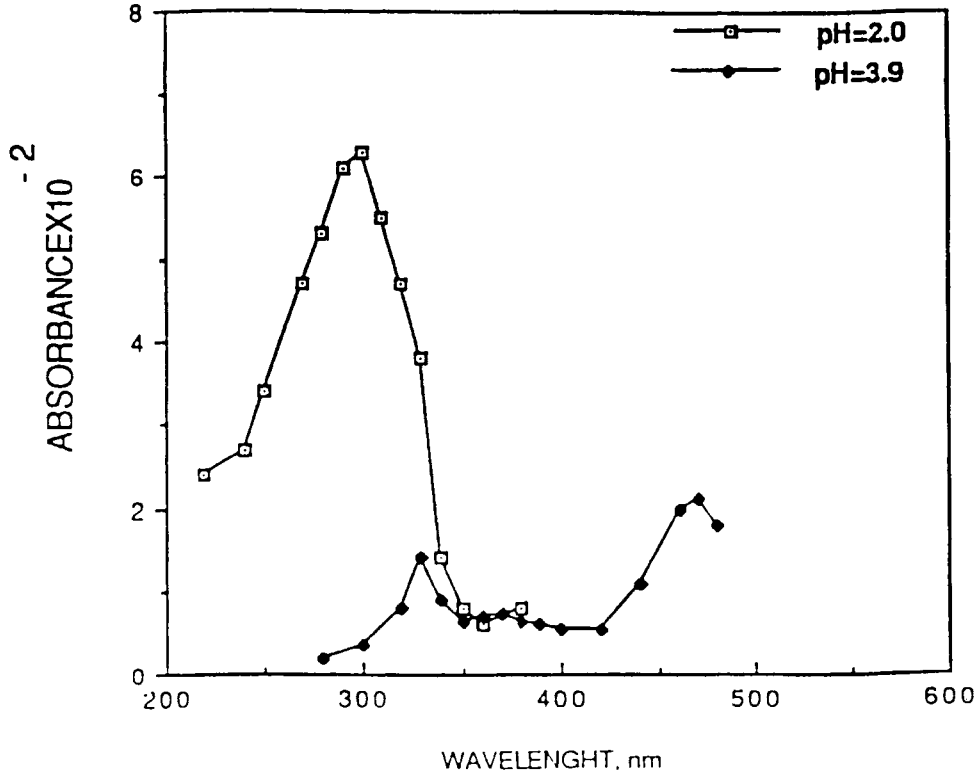
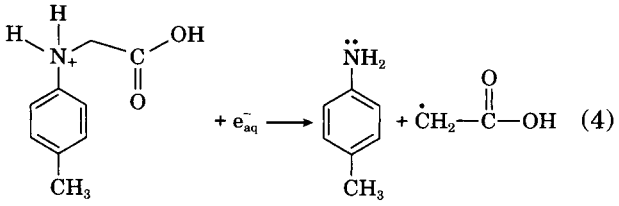


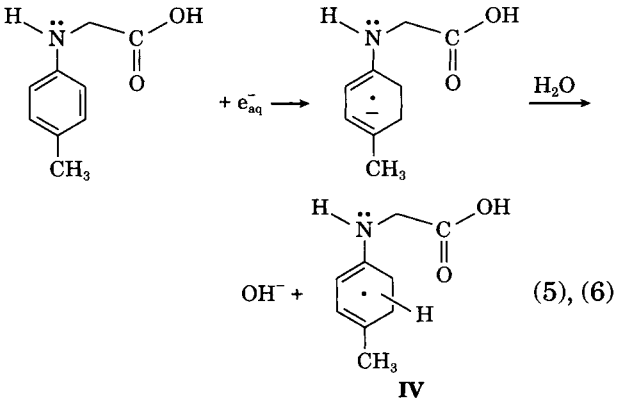
Figure 6 The transient absorption spectrum (2 ms after the pulse) of the pulsed N_2-saturated solution of 1.2 mol L^{-1} *t*-BuOH + 0.001 mol L^{-1} NTG. Dose = 15.0 Gy, pH = 2 and 3.9.

~ 50% of the electrons react with H_3O^+ to yield H atoms. H atoms react with NTG predominantly by addition to the aromatic ring. Therefore, at pH 3.9 the spectrum in Figure 6 results from reactions of both e^-_{aq} and H with NTG. Under these experimental conditions, the most probable reactions of e^-_{aq} with NTG are:

1. e^-_{aq} causing an amine elimination (reaction 4). At pH 3.9, some NTG molecules in the solution will be protonated. Therefore, e^-_{aq} will add to the protonated site that leads to the production of acetic acid free radicals and 4-methylaniline.



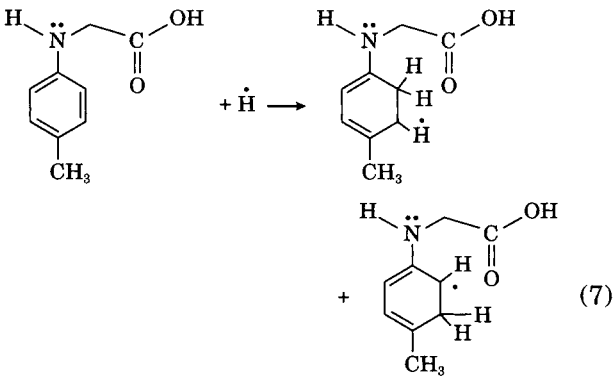
2. Some of the e^-_{aq} are captured by the aromatic rings to produce radical anions that rapidly react with water to produce cyclohexadienyl-type radicals according to reaction schemes (5) and (6).



IV

According to reaction (4), acetic acid free radicals should be produced in this system with a maximum absorption band at 330 nm. Because the extinction coefficient of acetic acid free radicals has been reported[24,25] at different pH values, one can calculate the fraction of e^-_{aq} reacting via reaction (4) and the fraction of e^-_{aq} reacting via reaction (5). In Figure 6, the maximum absorption bands of the acetic acid free radicals and the cyclohexadienyl radicals are overlapping. It should be mentioned that the absorption band of the acetic acid free radicals at pH 3–4 is at 320 nm.[25] Figure 6 shows a shift of +10 nm of the acetic acid free-radical absorption maximum band. This can be explained by the overlapping effect from the neighboring maximum absorption band of the cyclohexadienyl radical. The maximum absorption band of the cyclohexadienyl type radical that is produced from the reaction of e^-_{aq} with aniline is 355 nm, with an extinction coefficient of 4100 L mol^{-1} cm^{-1}.[26] The shift in the maximum absorption band of radical **IV** (reaction 6), 370 nm, from the reported cyclohexadienyl type radical produced from the reaction of aniline with e^-_{aq}, could be explained by the fact that radical **IV** has additional ring substituents. Based on ε = 4100 L mol^{-1} cm^{-1}, one can estimate the *G*-value of radical **IV** and, consequently, the ratio of reaction (4) to reaction (5), (6). It is approximately projected that two-thirds of e^-_{aq} react via reaction (4), while the remaining react via reaction (5), (6). Product analysis is needed to verify the foregoing result.

The reaction of H atoms with NTG was also studied in solutions containing *tert*-butyl alcohol (1.2 mol L^{-1}) at pH 2. At this pH most of the e^-_{aq} reacted with protons to form H atoms before reaction with NTG. The reaction of *t*-BuOH with H is very slow ($k = 8 \times 10^4$ L mol^{-1} s^{-1}), and most OH radicals react with *t*-BuOH with ($k = 5 \times 10^8$ L mol^{-1} s^{-1}).[17] The transient spectrum (Fig. 6) at pH 2 has a peak at 300 nm, which is characteristic of cyclohexadienyl radical.[17] As in the case of ȮH, H atoms are expected to add to the aromatic ring of NTG to produce cyclohexadienyl radicals (reaction 7).



Oxygen Uptake Measurements

To examine the involvement of oxygen in reactions with NTG radicals, oxygen uptake measurements were carried out under steady-state γ-radiolysis conditions. Figure 7 shows the effect of pH on $G(-O_2)$, the consumption of dissolved oxygen in micromoles/joule, in the radiolysis of 0.001 mol L^{-1} NTG solutions saturated with (4 : 1 v/v) N_2O/O_2. The small amount of H atoms ($G = 0.6 \times 10^{-7}$ mol

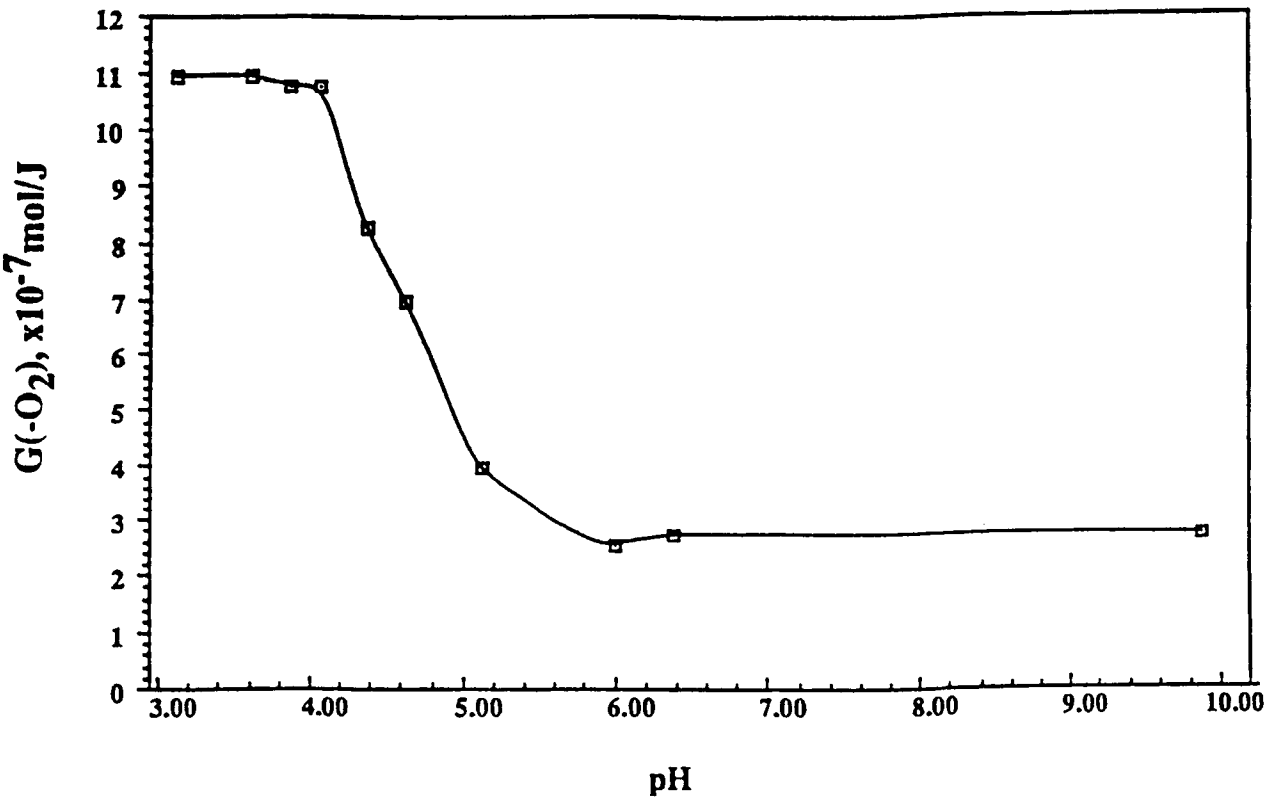


Figure 7 Oxygen consumption, $G(-O_2)$, as a function of pH in the γ radiolysis of 0.001 mol L^{-1} NTG solutions saturated with 4 : 1 v/v N_2O/O_2. Dose-rate = 1.2 Gy/min.

J^{-1}) react preferentially with oxygen[27] as in reaction (8).

$$\dot{H} + O_2 \xrightarrow{k=1.6\times10^{10}\ L\ mol^{-1}s^{-1}} HO_2^{\bullet} \qquad (8)$$

and the OH radicals react with NTG to produce OH adducts [reaction (1)] that subsequently react with O_2 [reaction (3)]. Both $HO_2^{\bullet}$ and the organic peroxyl radicals produced by reaction (3) disproportionate to recover half of the oxygen consumed; thus, $G(-O_2)$ is expected to be 3.2×10^{-7} mol J^{-1}. This can be explained by the fact that the total consumption of O_2 is equal to the total yield of carbon-centered free radicals (R$^{\bullet}$) plus the H atoms, that is, $5.8 \times 10^{-7} + 0.6 \times 10^{-7}$ mol J^{-1}). Hence, the total yield of the produced peroxyl radicals $RO_2^{\bullet}$ and $HO_2^{\bullet}$ is 6.4×10^{-7} mol J^{-1}. Peroxyl radicals can interact with themselves (bimolecularly) via Russel[28] or Bennett and Summers[29] mechanisms, as in reaction (9) or undergo $O_2^{\bar{}}$ elimination reactions as in reaction (10).[30]

$$2R\dot{O}_2 \rightarrow \text{products} + O_2 \qquad (9)$$

$$R\dot{O}_2 \rightarrow \text{products} + O_2^{\bar{}}. \qquad (10)$$

$HO_2^{\bullet}$ and superoxide radical ion ($O_2^{\bar{}}$) undergo the following reactions[31]:

$$2H\dot{O}_2 \rightarrow H_2O_2 + O_2 \qquad (11)$$

$$2\bar{O}_2 + 2\overset{+}{H} \rightarrow H_2O_2 + O_2. \qquad (12)$$

Consequently, up to half [$(6.4 \times 10^{-7}$ mol $J^{-1})/2$] of the O_2 consumed will be released. The results in Figure 7 clearly indicate a chain reaction at pH lower than about 5 with an apparent pK_a of about 4.8 because the value of $G(-O_2)$ is much higher than 6.4×10^{-7} mol J^{-1}. $HO_2^{\bullet}$ radicals have been suggested to be as active as other alkylperoxyl radicals and can abstract hydrogen atoms from weak C—H bonds, for example, bis-allylic hydrogens can be easily abstracted by $HO_2^{\bullet}$ radicals.[32]

The $HO_2^{\bullet}$ radical, in the dissociation equilibrium,[32]

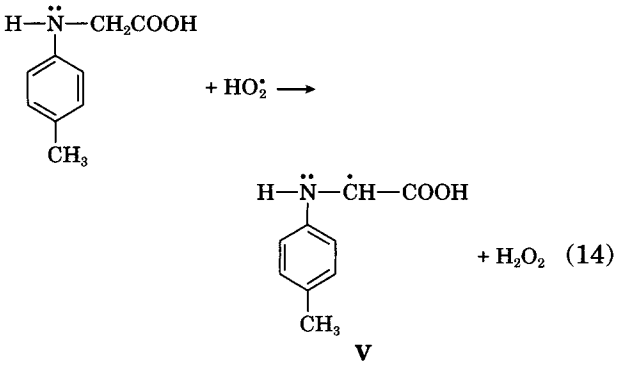
$$H\dot{O}_2 \rightleftharpoons O_2^{\bar{}} + H^+ \qquad (13)$$

has a pK_a of about 4.8.

Equation (13) can explain, at least in part, the pH dependence of $G(-O_2)$ in the γ radiolysis of

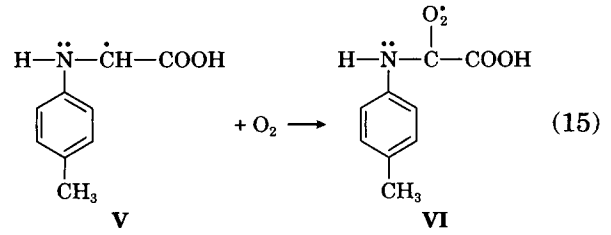
NTG. At low pH (below 4.8) $HO_2^{\cdot}$ radicals exist as the major form in the equilibrium concentration. At pH values higher than 4.8, $O_2^{\cdot-}$ is the predominant form in a steady-state concentration. Moreover, the pH dependence of $G(-O_2)$ (Fig. 7), has an apparent pK_a value of about 4.8.

Reaction (14) can be expected in this system at pH less than 4.8.



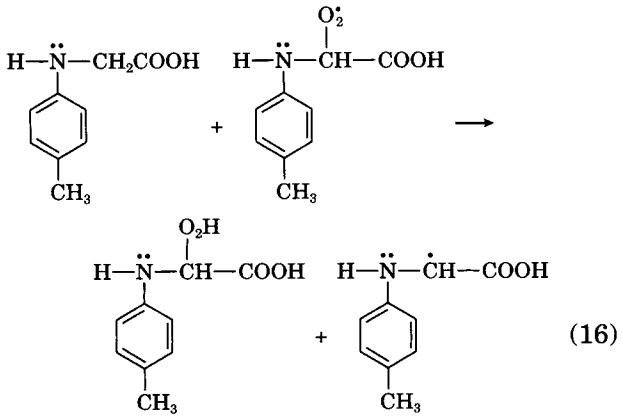
(14)

The resulting free radicals on the α-carbon atoms of the methylene groups in compound **V** should then react with oxygen to produce corresponding peroxyl radicals such as **VI** in reaction (15).



(15)

Chain peroxidation reactions may proceed via abstraction of hydrogen atoms from α positions by free radicals like **VI** (and subsequent reactions).



(16)

The results of $G(-O_2)$ strongly suggest that type **VI** peroxyl radicals can abstract H atoms from α positions and propagate chain reactions. In the case of superoxide radical ions that are formed above pH 4.8 [reaction (13)], there is no chain reaction because superoxide radical ions cannot abstract H atoms from α positions (Fig. 7).

CONCLUSIONS

The results of this study indicate that the oxidation of NTG by ȮH radicals, both in the presence and absence of oxygen, proceeds predominately via addition of ȮH to the aromatic ring and to the lone pair of nonbonding electrons on the nitrogen atom. ȮH addition to the lone pair of electrons on the nitrogen is followed by very fast OH^- elimination; ȮH addition to ring positions is followed by much slower OH^- elimination. These two OH^--elimination reactions lead to the production of $NTG^{+\cdot}$ radical cations. In the presence of oxygen, NTG$^{\cdot}$OH adducts react with oxygen to produce peroxyl radicals. The reaction of hydrated electrons with NTG yields NTG radical anions via addition to the phenyl ring and production of acetic acid free radicals and 4-methylaniline through a deamination reaction.

The O_2-uptake results demonstrate that $HO_2^{\cdot}$ can initiate a chain reaction with NTG: at low pH, (pH 3.9), $HO_2^{\cdot}$ may abstract H atoms from NTG at α positions. The resulting free radical (NTG$^{\cdot}$) may then react with oxygen to produce the corresponding peroxyl radicals $NTGO_2^{\cdot}$. The results also indicate that $NTGO_2^{\cdot}$ peroxyl radicals (**VI**) may propagate a chain reaction by abstracting labile hydrogen atoms from other NTG molecules. Some of these oxidative free-radical reactions may be relevant to understanding the role of NTG and similar *N*-aryl-α amino acids in initiating the free-radical polymerization of vinyl monomers as well as their chemical instability in oxygen environments.

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REFERENCES

1. R. L. Bowen, in Proc. Workshop on Adhesive Restorative Dental Materials, R. W. Phillips and G. Ryge, Eds., Indiana University, Owen Litho Service, Spencer, IN, 1961, pp. 177–191.

2. R. L. Bowen, *J. Dent. Res.*, **44,** 895–902 (1965).
3. R. L. Bowen, *J. Dent. Res.*, **44,** 903–905 (1965).
4. E. P. Plueddemann, In *Silane and Other Coupling Agents,* K. L. Mittal, Ed., VSP, Utrecht, The Netherlands, 1992, pp. 3–19.
5. R. L. Bowen, in *Dental Adhesive Materials,* H. D. Moskowitz, G. T. Ward, and E. D. Woolridge, Eds., Hunter–Bellevue School of Nursing, Prestige Graphic Services, New York, 1973, pp. 205–221.
6. S. Chaberek and A. E. Martell, Eds. *Organic Sequestering Agents,* John Wiley & Sons, Inc., New York, 1959, p. 378.
7. W. A. Zisman, in Proc. Workshop on Adhesive Restorative Dental Materials, R. W. Phillips and G. Ryge, Eds., Indiana University, Owen Litho Service, Spencer, IN, 1961, pp. 106–136.
8. J. M. Antonucci, J. W. Stansbury, and M. Farahani, *J. Dent. Res.*, **71,** 239 (1992).
9. R. L. Bowen, Department of Health and Human Services Public Health Service grant application, 1987, p. 25.
10. R. L. Bowen, E. N. Cobb, and D. N. Misra, *Ind. Eng. Chem. Prod. Res. Dev.*, **23,** 78–81 (1984).
11. R. L. Bowen and D. N. Misra, *J. Dent. Res.*, **65**(3), 412–416 (1986).
12. F. S. Dainton and D. B. Peterson, *Proc. Roy. Soc. London A,* **267,** 443–463 (1962).
13. E. P. L. Hunter, M. G. Simic, and B. D. Michael, *Rev. Sci. Instrum.*, **56,** 2199–2204 (1985).
14. M. Al-Sheikhly and M. G. Simic, *J. Phys. Chem.*, **93,** 3103–3106 (1989).
15. M. Anbar, D. Meyerstein, and P. Neta, *J. Phys. Chem.*, **70,** 2660–2662 (1966).
16. S. Steenken and P. O'Neil, *J. Phys. Chem.*, **82,** 372–374 (1978).
17. C. von Sonntag, *The Chemical Basis of Radiation Biology,* Taylor and Francis, New York, 1987, pp. 394 ff. and references cited therein.
18. Lin Qin, G. N. R. Tripathi, and R. H. Schuler, Z. Naturforsch., **40a,** 1026–1039 (1985).
19. P. Neta and R. W. Fessenden, *J. Chem. Phys.*, **78,** 523 (1976).
20. G. N. R. Tripathi and R. H. Schuler, *Chem. Phys. Lett.*, **110,** 542 (1984).
21. S. Gordon, K. H. Schmidt, and E. J. Hart, *J. Phys. Chem.*, **81**(2), 104–109 (1977).
22. A. Bryson, N. R. Davies, and E. P. Serjeant, *J. Am. Chem. Soc.*, **85,** 1933–1938 (1963).
23. J. P. Mittal and E. Hayon, *J. Phys. Chem.*, **78,** 1790–1794 (1974).
24. V. Marković, D. Nikolić, and O. I. Mićić, *Int. J. Radiat. Phys. Chem.*, **6,** 227–232 (1974).
25. P. Neta, M. Simic, and E. Hayon, *J. Phys. Chem.*, **73,** 4207–4213 (1969).
26. H. Christensen, *Int. J. Radiation Phys. Chem.*, **4,** 311–333 (1972).
27. M. Anbar, Farahataziz, and A. Ross, *Nat. Stand. Ref. Data Series* (U.S. National Bureau of Standards), 1975, NSRDS-NBS 51.
28. G. A. Russel, *J. Am. Chem. Soc.*, **79,** 1371–1377 (1957).
29. J. E. Bennett and R. Summers, *Can. J. Chem.*, **52,** 1377–1399 (1974).
30. E. Bothe, G. Behrens, and D. Schulte–Frohlinde, *Z. Naturforsch.*, **32b,** 886–889 (1977).
31. B. H. J. Bielski, *Photochem. Photobiol.*, **28,** 645–649 (1978).
32. J. M. Gebicki and B. H. Bielski, *J. Am. Chem. Soc.*, **103,** 7020–7022 (1981).

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