Free Rad. Res. Comms., Vol. 6, No. 2-3, pp. 109-110
Reprints available directly from the publisher
Photocopying permitted by license only

FREE RADICAL GENERATION BY ULTRASOUND IN AQUEOUS SOLUTIONS OF DNA CONSTITUENTS

TAKASHI KONDO, C. MURALI KRISHNA and PETER RIESZ

Radiation Oncology Branch, NCI; National Institutes of Health Bethesda, MD 20892 USA

In recent years the sonochemistry of aqueous solutions has been studied extensively by Henglein, Hart and co-workers[1-3] while that of organic liquids has been investigated by Suslick *et al.*[4]

Both continuous and pulsed ultrasound above a certain intensity threshold lead to stable and transient acoustic cavitation.[5] During the collapse of transient cavitation bubbles, very high local temperatures (several thousand degrees Kelvin) and high pressures are generated which result in the thermal decomposition of water vapour into hydrogen atoms and hydroxyl radicals which were detected by spin trapping and electron spin resonance.[6,7]

The sonolysis of liquids can be explained in terms of reactions occurring in three different regions. First, in the high temperature region of the collapsing gas bubbles, typical combustion reactions have been observed. These include isotopic exchange between deuterium gas and methane[2] and the thermal decomposition of methanol to methyl radicals. Methyl radicals and CH_2OH radicals as well as the isotopically mixed radicals CH_2D and CHD_2 were observed when the sonolysis of CH_3OD:D_2O solutions was studied.[8]

The second region of interest is the interface between hot gas bubbles and the cool bulk solvent. In this region, large temperature and pressure gradients exist and its unknown characteristics are objectives of sonochemical studies. For organic liquids, Suslick *et al.*[4] have calculated a temperature of about 1900 K in a spherical shell with a width of about 200 nm.

Henglein and Kormann[9] have shown that in aqueous solutions OH radicals are scavenged by volatile radical scavengers with an efficiency which is not determined by the specific rate constants known from radiation chemistry but by other factors, prinicipally the hydrophobicity of the solutes. The effect of non-volatile scavengers on OH radical induced thymine radicals as measured by spin trapping were found to parallel their rate constants with OH radicals.[10]

The spin trap 3,5-dibromo-4-nitrosobenzene sulfonate (DBNBS) was found to be particularly suitable for sonolysis studies of aqueous solutions. The sulfonate group ensures non-volatility and solubility and several carbon-centered radical spin adducts show sufficiently detailed spectra to allow the identification of the trapped radicals. The sonolysis of argon-saturated dilute solutions of amino acids,[11] nucleic acid bases and nucleosides,[12] and of various dihydro and alkyl substituted pyrimidines[13] was investigated with DBNBS as the spin trap.

Spin adducts were also generated by OH radicals produced by UV-photolysis of aqueous solutions containing hydrogen peroxide and the non-volatile solute of interest. For dilute solutions (< 0.1 M) of amino acids and of nucleic acid constituents, the ESR spectra of the spin adducts were identical for photolysis in the presence of H_2O_2 and for sonolysis.[11-13] These results indicate that radicals from amino acids, dipeptides and nucleic acid constituents were formed by H and OH radicals which lead to H-abstraction reactions and addition to the C5-C6 double bond of pyrimidines.

Recently we studied the sonolysis of sodium acetate, amino acids and several sugars (including 2-deoxy-D ribose) over a wide range of concentrations. At high concentrations (> 0.2 M), new radicals (typically methyl radicals which are formed in the high temperature interface region were spin trapped.[14] In general, pyrolysis radicals can be detected when non-volatile solutes are present at high concentrations in the interface region of cavitation bubbles.

References

1. Henglein, A. Sonochemistry: historical developments and modern aspects. *Ultrasonics*, **25**, 6, (1987).
2. Hart, E.J. and Henglein, A. Isotopic Exchange in the Sonolysis of Aqueous Solutions Containing D_2 and CH_4. *J. Phys. Chem.*, **91**, 4166, (1987).
3. Gutiérrez, M., Henglein, A. and Fischer, Ch.H. Hot spot kinetics of the sonolysis of aqueous acetate solutions. *Int. J. Radiat. Biol.*, **50**, 313, (1986).
4. Suslick, K.S., Hammerton, D.A. and Cline Jr., R.E. The sonochemical hot spot. *J. Am. Chem. Soc.*, **198**, 5641, (1986).
5. Flynn, H.G. In *Physical Acoustics: Principles and Methods* Mason, W.P. (ed.). Academic Press, New York 1964, p. 165, (1964).
6. Makino, K., Mossoba, M.M. and Riesz. P. Chemical effects of ultrasound on aqueous solutions. Formation of hydroxyl radicals and hydrogen atoms. *J. Phys. Chem.*, **87**, 1369, (1983).
7. Christman, C.L., Carmichael, A.J., Mossoba, M.M. and Riesz, P. *Ultrasonics*, **25**, 31, (1987).
8. Murali Krishna, C., Lion, Y., Kondo, T. and Riesz, P. Thermal decomposition of methanol in the sonolysis of methanol-water mixtures. Spin-trapping evidence for isotope exchange reactions. *J. Phys. Chem.*, **91**, 5847, (1987).
9. Henglein, A. and Kormann, C. Scavenging of OH radicals produced in the sonolysis of water, *Int. J. Radiat. Biol.*, **48**, 251, (1985).
10. Kondo, T., Murali Krishna, C. and Riesz, P. Effect of non-volatile scavengers of hydroxyl radicals on thymine radical formation induced by gamma-rays and ultrasound. *Int. J. Radiat. Biol.*, **53**, 891, (1988).
11. Murali Krishna, C., Kondo, T. and Riesz, P. Sonochemistry of aqueous solutions of amino acids and peptides. A spin trapping study, *Radiat. Phys. Chem.*, **32**, 121, (1988).
12. Kondo, T., Murali Krishna, C. and Riesz, P. Free radical generation by ultrasound in aqueous solutions of nucleic acid bases and nucleosides: an ESR and spin-trapping study, *Int. J. Radiat. Biol.*, **53**, 331, (1988).
13. Kondo, T., Murali Krishna, C. and Riesz, P. Sonolysis, radiolysis, and hydrogen peroxide photolysis of pyrimidine derivatives in aqueous solutions: A spin trapping study, *Radiat. Res.* (in press).
14. Kondo, T., Murali Krishna, C. and Riesz. P. (unpublished).