



<http://researchspace.auckland.ac.nz>

ResearchSpace@Auckland

Copyright Statement

The digital copy of this thesis is protected by the Copyright Act 1994 (New Zealand).

This thesis may be consulted by you, provided you comply with the provisions of the Act and the following conditions of use:

- Any use you make of these documents or images must be for research or private study purposes only, and you may not make them available to any other person.
- Authors control the copyright of their thesis. You will recognise the author's right to be identified as the author of this thesis, and due acknowledgement will be made to the author where appropriate.
- You will obtain the author's permission before publishing any material from their thesis.

To request permissions please use the Feedback form on our webpage.

<http://researchspace.auckland.ac.nz/feedback>

General copyright and disclaimer

In addition to the above conditions, authors give their consent for the digital copy of their work to be used subject to the conditions specified on the Library Thesis Consent Form.

THE RADIOLYSIS OF AQUEOUS SOLUTIONS OF CYSTEINE

by

Robert V. Winchester

A Thesis presented to the University of Auckland
for the Degree of Doctor of Philosophy.

July 1968.

For BREND A.

BOND

MADE IN BRITAIN

ACKNOWLEDGEMENTS

I wish to thank most sincerely my Supervisor, Dr J. E. Packer, for his interest in this work and the guidance he has given me.

The assistance of the following persons or organizations is also gratefully acknowledged:-

Members of the Technical Staff, and in particular Mr W. Barr for his expert glassblowing,

Chemistry Division, D.S.I.R., Auckland, and Dr G. S. McNaughton, of the Institute of Nuclear Sciences, Lower Hutt, for chemicals, The University Grants Committee, for the award of a Post-graduate Scholarship, and the United States Air Force Office of Scientific Research for funds for the purchase of the source and spectrophotometer,

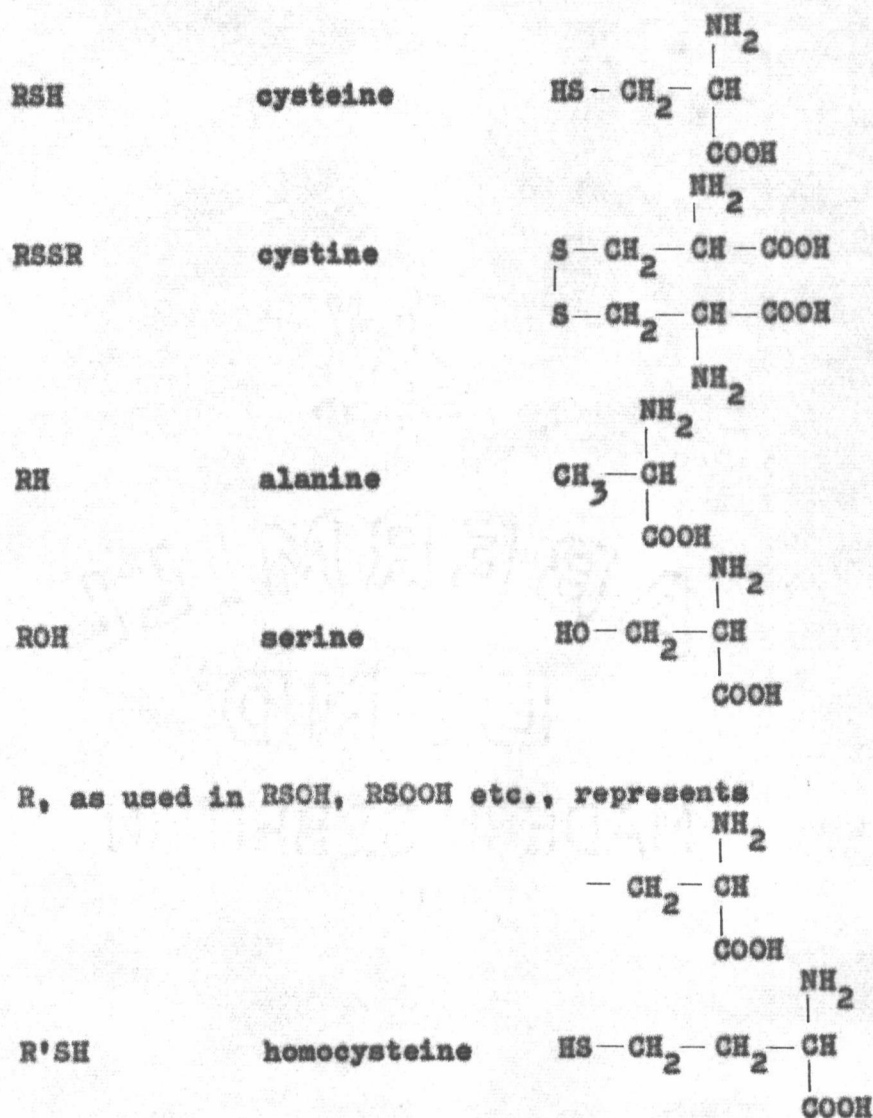
Mr J. P. Barton for some interesting discussions,

Candice Beresford for typing this thesis.

Finally I would like to record my appreciation to my wife Brenda for assistance in more ways than can be enumerated here, but particularly for her forbearance during the preparation of this thesis. To her it is dedicated.

NOTE

Throughout this thesis the following abbreviated formulae are used for convenience:-



ABSTRACT

The radiolysis of cysteine in both deaerated and oxygenated solution at pH 7 has been studied.

In deaerated solution the mechanism of the reaction appears to be the same as that at pH 5 - 6. The rate constant for the reaction



has been measured by competition with paranitrosodimethylaniline. A value of 9×10^9 was found, which though not absolutely accurate (for reasons described in the text) is sufficiently accurate to show that the reaction is fast. The rate constant of the reaction



has been measured by competition with oxygen, and a value of $(4.0 \pm 0.2) \times 10^9$ was found. This compares well with values found by other methods.

From the values of $G(-\text{RSH})$, $G(\text{RSSR})$, and $G(\text{H}_2\text{O}_2)$ in oxygenated solution, and from the effects of the scavengers nitrous oxide and acetone on these values a mechanism has been proposed in which RS radicals produced by attack of primary species on cysteine propagate a chain, the rate of the propagation reaction depending on the cysteine concentration.

The autoxidation of cysteine has been studied briefly, the rate being found proportional to oxygen concentration. The mechanism is believed to be the same as that for the radiolysis.

Copyright © 2004 John Wiley & Sons, Ltd.

10

Chapter 1	<u>Introduction to Radiation Chemistry</u>	
1.1	Action of Ionizing Radiation on Matter	1
1.2	Radiation Chemistry of Aqueous Solutions	4
1.3	Chemical Protection Against Radiation Effects	10
1.31	Action of Protective Compounds	13
Chapter 2	<u>Previous Work</u>	
2.1	Autoxidation of Cysteine	16
2.2	Oxidation by Hydrogen Peroxide	19
2.3	Radiolysis of Cysteine	19
Chapter 3	<u>Experimental</u>	
3.1	Materials and Preparation	
3.11	Materials	30
3.12	Preparation of Solutions	30
3.2	Procedure	
3.21	Addition of Gases and Irradiation Procedure	33
3.22	Dosimetry	38
3.221	Calculation of G Values	40
3.23	Autoxidation	41
3.3	Analytical Methods	
3.31	Cysteine Analysis	43
3.311	Phosphotungstic Acid Method	43
3.312	N-ethylmaleimide Method	45
3.313	DTNB Method	45
3.32	Cystine Analysis	46
3.321	Phosphotungstic Acid Method	46
3.322	N-ethylmaleimide Method	46
3.323	Direct Method	48
3.33	Hydrogen Sulphide Analysis	50
3.34	Hydrogen peroxide Analysis	52
3.35	p-nitrosodimethylaniline Analysis	56
3.36	Chromatography	56
Chapter 4	<u>Results and Discussion - Part A</u>	
4.1	Autoxidation of Cysteine	58
4.11	Cysteine-hydrogen peroxide Reaction	61

4.2	Results over Large Dose-range	63
4.21	Discussion	69
4.3	Radiolysis of Cysteine in Deoxygenated Solution	71
4.31	Concentration Effects	79
<u>Chapter 5</u>	<u>Results and Discussion - Part B</u>	
5.1	Oxygenated solutions	
5.11	Competition for Hydrated Electrons	84
5.12	Competition for the Hydroxyl Radical	85
5.2	Yields in Oxygenated Solution in the absence and presence of Scavengers	
5.21	Results	93
5.22	Discussion	112
	5.221 Effects of Acetone and nitrous oxide	125
	5.222 Other Features of the Reaction	129
5.3	Solutions containing Thallous ions	133
<u>Summary</u>		143
<u>Appendix</u>		148
<u>References</u>		153

LIST OF FIGURES

	Page
3.1 Irradiation vessels	34
3.2 Adaptors for irradiation vessels	35
3.3 Vacuum line	37
3.4 Removal of hydrogen sulphide from solution	37
3.5 Autoxidation vessel	42
3.6 Calibration graph for cystine analysis	49
3.7 Calibration graph for hydrogen sulphide analysis	53
3.8 Calibration graph for hydrogen peroxide analysis	55
4.1 Cysteine loss by autoxidation	60
4.2 Cysteine - H_2O_2 reaction	62
4.3 Cysteine loss at high doses in oxygenated solution	65
4.4 Cystine production at high doses in oxygenated solution	66
4.5 H_2S production at high doses in oxygenated solution	67
4.6 Cysteine loss in deaerated solution	72
4.7 Cystine production in deaerated solution	73
4.8 H_2S production in deaerated solution	74
4.9 H_2O_2 production in deaerated solution	75
5.1 H_2S production in oxygenated solution	86
5.2 Competition plot from data in Figure 5.1	87
5.3 Loss of p-nitrosodimethylaniline in N_2O saturated solution	90
5.4 Competition plot from data in Figure 5.2	92
5.5 Dose-rate effect on cysteine loss and cystine production in oxygenated solution	99
5.6 Cysteine loss in oxygenated solution for $3 \times 10^{-3} M$ RSH	100
5.7 Cysteine loss in oxygenated solution for $5 \times 10^{-4} M$ RSH	102
5.8 Cystine production in oxygenated solution	103
5.9 H_2O_2 production in oxygenated solution	104
5.10 Concentration effect on cysteine loss in oxygenated solution	106
5.11 Concentration effect on cystine production in oxygen- ated solution	107
5.12 Concentration effect on H_2S production in oxygenated solution	108
5.13 Concentration effect on H_2O_2 production in oxygenated solution	109

	Page
5.14 Cysteine loss with N_2O and acetone as scavengers	110
5.15 H_2O_2 production with N_2O and acetone as scavengers	111
5.16 Cysteine loss with thallous ion as scavenger	135
5.17 H_2O_2 production with thallous ion as scavenger	136
6 Proposed reaction scheme for cysteine radiolysis	146