

# Table of contents

## Radical reaction rates in liquids

### Part c: Radicals centered on N, S, P and other heteroatoms. Nitroxyls

#### General introduction

H. Fischer, Physikalisch-Chemisches Institut der Universität Zürich, Switzerland

A Definition and coverage . . . . .	1
B Arrangement and contents of tables . . . . .	1
C Important monographs, series, compilations . . . . .	2
D Symbols and abbreviations . . . . .	3

#### 5 Nitrogen-centered radicals

K. U. Ingold, National Research Council Canada, Division of Chemistry, Ottawa, Canada

5.0 Introduction . . . . .	5
5.1 Aminyl radicals, RR'N <sup>•</sup> . . . . .	6
5.1.1 Bimolecular self-reactions and radical-dimer equilibria . . . . .	6
5.1.1.1 Monoalkylaminyls (R=alkyl, R'=H) . . . . .	6
5.1.1.2 Acyclic dialkylaminyls (R, R'=alkyl) . . . . .	6
5.1.1.3 Cyclic aminyls (R, R', and N form a ring) . . . . .	7
5.1.1.4 Monoarylaminyls (R=aryl, R'=H) . . . . .	9
5.1.1.5 Acyclic alkarylaminyls (R=alkyl, R'=aryl) . . . . .	10
5.1.1.6 Acyclic diarylaminyls (R, R'=aryl) . . . . .	11
5.1.2 Reactions with a different radical . . . . .	14
5.1.2.1 Monoalkylaminyls (R=alkyl, R'=H) . . . . .	14
5.1.2.2 Cyclic aminyls (R, R', and N form a ring) . . . . .	14
5.1.3 Unimolecular reactions . . . . .	15
5.1.3.1 Acyclic dialkylaminyls (R, R'=alkyl) . . . . .	15
5.1.3.2 Acyclic aminyls with leading atom of R and/or R' a heteroatom . . . . .	17
5.1.3.3 Cyclic aminyls (R, R', and N form a ring) . . . . .	18
5.1.4 Intermolecular hydrogen atom abstractions from carbon . . . . .	20
5.1.4.1 Aminyl (R, R'=H) . . . . .	20
5.1.4.2 Acyclic dialkylaminyls (R, R'=alkyl) . . . . .	21
5.1.4.3 Acyclic aminyls with leading atom of R and/or R' a heteroatom . . . . .	22
5.1.4.4 Cyclic aminyls (R, R', and N form a ring) . . . . .	22
5.1.4.5 Acyclic diarylaminyls (R, R'=aryl) . . . . .	23
5.1.5 Intermolecular hydrogen atom abstractions from oxygen . . . . .	25
5.1.5.1 Aminyl (R, R'=H) . . . . .	25
5.1.5.2 Cyclic aminyls (R, R', and N form a ring) . . . . .	26
5.1.5.3 Acyclic alkarylaminyls (R=alkyl, R'=aryl) . . . . .	26
5.1.5.4 Acyclic diarylaminyls (R, R'=aryl) . . . . .	26
5.1.6 Intermolecular hydrogen atom abstractions from nitrogen; aminyl (R, R'=H) . . . . .	28

5.1.7 Intermolecular hydrogen atom abstractions from sulfur . . . . .	28
5.1.7.1 Monoalkylaminyls ( $R = \text{alkyl}$ , $R' = \text{H}$ ) . . . . .	28
5.1.7.2 Acyclic diarylaminyl ( $R, R' = \text{aryl}$ ) . . . . .	29
5.1.8 Intermolecular reactions other than hydrogen atom abstraction . . . . .	29
5.1.8.1 Aminyl ( $R, R' = \text{H}$ ) . . . . .	29
5.1.8.2 Acyclic dialkylaminyls ( $R, R' = \text{alkyl}$ ) . . . . .	32
5.1.8.3 Cyclic aminyls ( $R, R'$ , and N form a ring) . . . . .	33
5.1.8.4 Monoarylaminyls ( $R = \text{aryl}$ , $R' = \text{H}$ ) . . . . .	35
5.1.8.5 Acyclic diarylaminyl ( $R, R' = \text{aryl}$ ) . . . . .	36
5.2 Aminium radicals, $\text{RR}'\text{R}''\text{N}^+$ . . . . .	36
5.2.1 Bimolecular self-reactions and radical-dimer equilibria . . . . .	36
5.2.1.1 Acyclic dialkylaminiums ( $R, R' = \text{alkyl}$ , $R'' = \text{H}$ ) . . . . .	36
5.2.1.2 Secondary cyclic aminiums ( $R, R'$ , and N form a ring, $R'' = \text{H}$ ) . . . . .	37
5.2.1.3 Acyclic trialkylaminiums ( $R, R', R'' = \text{alkyl}$ ) . . . . .	39
5.2.1.4 Acyclic triarylaminiums ( $R, R', R'' = \text{aryl}$ ) . . . . .	39
5.2.2 Reactions with a different radical . . . . .	45
5.2.2.1 Tertiary cyclic aminiums ( $R, R'$ , and N form a ring, $R'' = \text{alkyl}$ ) . . . . .	45
5.2.2.2 Monoarylaminiums ( $R = \text{aryl}$ , $R', R'' = \text{H}$ ) . . . . .	45
5.2.3 Unimolecular reactions . . . . .	45
5.2.3.1 Aminium ( $R, R', R'' = \text{H}$ ) . . . . .	45
5.2.3.2 Monoalkylaminiums ( $R = \text{alkyl}$ , $R', R'' = \text{H}$ ) . . . . .	46
5.2.3.3 Acyclic dialkylaminiums ( $R, R' = \text{alkyl}$ , $R'' = \text{H}$ ) . . . . .	46
5.2.3.4 Secondary cyclic aminiums ( $R, R'$ , and N form a ring, $R'' = \text{H}$ ) . . . . .	47
5.2.3.5 Acyclic trialkylaminiums ( $R, R', R'' = \text{alkyl}$ ) . . . . .	48
5.2.3.6 Tertiary cyclic aminiums ( $R, R'$ , and N form a ring, $R'' = \text{alkyl}$ ) . . . . .	50
5.2.3.7 Monoarylaminiums ( $R = \text{aryl}$ , $R', R'' = \text{H}$ ) . . . . .	51
5.2.4 Intermolecular hydrogen atom abstraction from carbon . . . . .	52
5.2.4.1 Aminium ( $R, R', R'' = \text{H}$ ) . . . . .	52
5.2.4.2 Monoalkylaminiums ( $R = \text{alkyl}$ , $R', R'' = \text{H}$ ) . . . . .	53
5.2.4.3 Acyclic dialkylaminiums ( $R, R' = \text{alkyl}$ , $R'' = \text{H}$ ) . . . . .	54
5.2.4.4 Secondary cyclic aminiums ( $R, R'$ , and N form a ring, $R'' = \text{H}$ ) . . . . .	67
5.2.4.5 Acyclic trialkylaminiums ( $R, R', R'' = \text{alkyl}$ ) . . . . .	72
5.2.4.6 Tertiary cyclic aminiums ( $R, R'$ , and N form a ring, $R'' = \text{alkyl}$ or forms a second ring) . . . . .	73
5.2.5 Intermolecular reactions other than hydrogen atom abstraction . . . . .	74
5.2.5.1 Aminium ( $R, R', R'' = \text{H}$ ) . . . . .	74
5.2.5.2 Acyclic dialkylaminiums ( $R, R' = \text{alkyl}$ , $R'' = \text{H}$ ) . . . . .	75
5.2.5.3 Secondary cyclic aminiums ( $R, R'$ , and N form a ring, $R'' = \text{H}$ ) . . . . .	76
5.2.5.4 Tertiary cyclic aminiums ( $R, R'$ , and N form a ring, $R'' = \text{alkyl}$ or aryl) . . . . .	77
5.2.5.5 Tertiary arylaminium ( $R, R', R'' = \text{aryl}$ ) . . . . .	79
5.3 Carboxamidyl radicals, $\text{R}'\text{CO}\dot{\text{N}}\text{R}$ . . . . .	79
5.3.1 Bimolecular self-reactions . . . . .	79
5.3.1.1 Acyclic acylalkylaminyls ( $R, R' = \text{alkyl}$ ) and alkyl(alkoxycarbonyl)aminyls ( $R = \text{alkyl}$ , $R' = \text{alkoxy}$ ) . . . . .	79
5.3.1.2 Acyclic acylarylthioaminyls ( $R = \text{alkyl}$ , $R' = \text{arylthio}$ ) . . . . .	81
5.3.2 Intramolecular hydrogen atom abstractions . . . . .	81
5.3.2.1 Acylaminyls ( $R = \text{H}$ , $R' = \text{alkyl}$ ) . . . . .	81
5.3.2.2 Acyclic acylalkylaminyls ( $R, R' = \text{alkyl}$ ) and alkyl(alkoxycarbonyl)aminyls ( $R = \text{alkyl}$ , $R' = \text{alkoxy}$ ) . . . . .	82
5.3.3 Intramolecular additions to a multiple bond . . . . .	83
5.3.3.1 Acyclic acylalkylaminyls ( $R, R' = \text{alkyl}$ or alkenyl) . . . . .	83
5.3.3.2 Acyclic aroylalkylaminyls ( $R = \text{alkyl}$ , $R' = \text{aryl}$ ) . . . . .	85
5.3.4 Other unimolecular reactions . . . . .	85
5.3.5 Intermolecular hydrogen atom abstractions from carbon . . . . .	86
5.3.5.1 Acyclic acylalkylaminyls ( $R, R' = \text{alkyl}$ ) . . . . .	86
5.3.5.2 Cyclic acylalkylaminyls ( $R, R'\text{CO}$ , and N form a ring) . . . . .	87
5.3.6 Intermolecular reactions other than hydrogen atom abstraction, acyclic acylalkylaminyls ( $R, R' = \text{alkyl}$ ) . . . . .	89

5.4 Sulfinamidyl radicals, RR'SON·, and sulfonamidyl radicals, RR'SO <sub>2</sub> N· . . . . .	89
5.4.1 Bimolecular self-reactions and first-order decays . . . . .	89
5.4.2 Intermolecular hydrogen atom abstractions from carbon . . . . .	92
5.5 Imidyl radicals, RCOR'CON· . . . . .	93
5.5.1 Unimolecular reactions . . . . .	93
5.5.2 Intermolecular hydrogen atom abstractions from carbon . . . . .	93
5.5.3 Intermolecular hydrogen atom abstractions from carbon vs. intermolecular additions to C—C multiple bonds (relative) . . . . .	96
5.5.4 Intermolecular additions to C—C multiple bonds . . . . .	97
5.5.5 S <sub>H</sub> 2 reactions with tetraalkylstannanes . . . . .	97
5.6 Iminyl radicals, RR'C=N· . . . . .	98
5.6.1 Bimolecular self-reactions . . . . .	98
5.6.1.1 Iminyl (R, R'=H) . . . . .	98
5.6.1.2 Monoalkyliminyls (R = alkyl, R'=H) . . . . .	99
5.6.1.3 Acyclic dialkyliminyls (R, R'=alkyl, including CF <sub>3</sub> ) . . . . .	99
5.6.1.4 Cyclic iminyls (R, R', and C form a ring) . . . . .	99
5.6.1.5 Acyclic diaryliminyls (R, R'=aryl) . . . . .	100
5.6.2 Unimolecular reactions . . . . .	100
5.6.2.1 Acyclic dialkyliminyls (R, R'=alkyl) . . . . .	100
5.6.2.2 Cyclic iminyls (R, R', and C form a ring) . . . . .	101
5.6.2.3 Alkaryl and diaryliminyls (R = aryl, R'=alkyl or aryl) . . . . .	101
5.6.3 Intermolecular hydrogen atom abstractions from carbon . . . . .	101
5.7 Alkoxyaminyl radicals, RR'ON· . . . . .	102
5.7.1 Bimolecular self-reactions and radical-dimer equilibria . . . . .	102
5.7.1.1 Hydroxyaminyl (R, R'=H) . . . . .	102
5.7.1.2 Alkoxyaminyls (R = H, R'=alkyl) . . . . .	102
5.7.1.3 Alkoxyalkylaminyls (R, R'=alkyl) . . . . .	102
5.7.1.4 Alkoxyarylaminyls (R = aryl, R'=alkyl) . . . . .	103
5.7.2 Unimolecular reactions . . . . .	103
5.7.2.1 Alkoxyalkylaminyl (R, R'=alkyl) . . . . .	103
5.7.2.2 Alkoxyaminyls, with leading atom of R a heteroatom . . . . .	103
5.7.3 Intermolecular hydrogen atom abstraction from oxygen . . . . .	104
5.8 Thioaminyl radicals, RR'SN· . . . . .	104
5.8.1 Bimolecular self-reactions and radical-dimer equilibria . . . . .	104
5.8.1.1 Arylthioalkylaminyls (R = alkyl, R'=aryl) . . . . .	104
5.8.1.2 Alkylthioarylaminyls (R = aryl, R'=alkyl) . . . . .	104
5.8.1.3 Arylthioarylaminyls (R, R'=aryl) . . . . .	105
5.8.2 Unimolecular reactions . . . . .	107
5.8.2.1 Alkylthioalkylaminyl (R, R'=alkyl) . . . . .	107
5.8.2.2 Aminothiylalkylaminyls (R = alkyl, leading atom of R'=N) . . . . .	107
5.8.3 Intermolecular reactions with molecules . . . . .	108
5.9 Dithioaminyl radicals, RSR'SN· . . . . .	108
5.9.1 Bimolecular self-reactions and radical-dimer equilibria . . . . .	108
5.9.1.1 Cyclic dithioaminyls (RS, R'S, and N form a ring) . . . . .	108
5.9.1.2 Diarylthioaminyls (R, R'=aryl) . . . . .	109
5.9.2 Intermolecular reactions with molecules . . . . .	109
5.10 Hydrazyl radicals, R'R"NNR· . . . . .	110
5.10.1 Bimolecular self-reactions and radical-dimer equilibria . . . . .	110
5.10.1.1 Hydrazyl (R, R', R"=H) . . . . .	110
5.10.1.2 Monoalkylhydrazyls (R = alkyl, R', R"=H) . . . . .	110
5.10.1.3 Acyclic dialkylhydrazyls (R = H, R', R"=alkyl) . . . . .	110
5.10.1.4 Acyclic dialkylhydrazyls (R, R'=alkyl, R"=H) . . . . .	111
5.10.1.5 Cyclic dialkylhydrazyls (R = H, R', R" and the N to which they are attached form a ring) . . . . .	111
5.10.1.6 Acyclic trialkylhydrazyls (R, R', R"=alkyl, including CF <sub>3</sub> ) . . . . .	112

5.10.1.7 Cyclic trialkylhydrazyls and related species ( $R = \text{alkyl}$ , $R'$ , $R''$ and the N to which they are attached form a ring or, $R' = \text{alkyl}$ , $R$ , N, N, and $R''$ form a ring) . . . . .	112
5.10.1.8 Acyclic diarylhydrazyls ( $R$ , $R' = \text{aryl}$ , or similar group, $R'' = \text{H}$ ) . . . . .	113
5.10.1.9 Diarylaroylhydrazyls ( $R = \text{aroyl}$ , $R'$ , $R'' = \text{aryl}$ ) . . . . .	116
5.10.2 Reactions with a different radical . . . . .	120
5.10.3 Unimolecular reactions . . . . .	120
5.10.3.1 Cyclic trialkylhydrazyls ( $R = \text{alkyl}$ , $R'$ , $R''$ , and the N to which they are attached form a ring) . . . . .	121
5.10.3.2 Cyclic trialkylhydrazyls ( $R$ , $R'$ , N and N form a ring, $R'' = \text{alkyl}$ ) . . . . .	121
5.10.3.3 Tri-substituted hydrazyls with leading atom of R and/or $R'$ , $R''$ a heteroatom . . . . .	122
5.10.3.4 Acyclic triarylhydrazyls ( $R$ , $R'$ , $R'' = \text{aryl}$ ) . . . . .	122
5.10.4 Intermolecular hydrogen atom abstractions by DPPH from hydrocarbons . . . . .	123
5.10.5 Intermolecular hydrogen atom abstractions by DPPH from amines . . . . .	123
5.10.6 Intermolecular hydrogen atom abstractions by DPPH from phenols . . . . .	126
5.10.7 Intermolecular hydrogen atom abstractions by DPPH from thiols . . . . .	142
5.10.8 Intermolecular hydrogen atom abstractions by DPPH from ethers . . . . .	145
5.10.9 Intermolecular hydrogen atom abstractions by DPPH from acids, alcohols, anhydrides and other compounds . . . . .	146
5.10.10 DPPH-solvent association equilibria . . . . .	147
5.11 Hydrazyl radical cations, $(R'R''NNR_2)_+^+$ , and related species . . . . .	147
5.11.1 Bimolecular self-reactions . . . . .	147
5.11.2 Reactions with a different radical . . . . .	148
5.11.3 Unimolecular reactions . . . . .	149
5.11.4 Intermolecular reactions with molecules . . . . .	150
5.12 Verdatyl and related radicals . . . . .	151
5.12.1 Bimolecular self-reactions . . . . .	151
5.12.2 Reactions with a different radical . . . . .	151
5.12.3 Intermolecular reactions with molecules . . . . .	152
5.13 Diazirinyl radicals, $\overline{RC-N-N}$ . . . . .	154
5.13.1 Bimolecular self-reactions . . . . .	154
5.13.1.1 Alkyldiazirinyl ( $R = \text{alkyl}$ ) . . . . .	154
5.13.1.2 Aryldiazirinyl ( $R = \text{aryl}$ ) . . . . .	154
5.14 Diazenyl radicals, $RN=N$ . . . . .	155
5.14.1 Bimolecular self-reactions . . . . .	155
5.14.2 Unimolecular reactions . . . . .	155
5.14.3 Other reactions . . . . .	156
5.15 Azidyl radical, $N_3^-$ . . . . .	156
5.15.1 Bimolecular self-reactions . . . . .	156
5.15.2 Other reactions . . . . .	156
5.16 Triazenyl radicals, $R_2N_3^{\cdot}$ , and diazaallyl radicals, $(RN)_2\dot{C}R'$ ; bimolecular self-reactions . . . . .	157
5.17 Benzolnitrile radical anions, $ArCM^-$ : unimolecular reactions . . . . .	158
References for 5.1...5.17 . . . . .	160

## 6 Aminoxy and related radicals

K. U. Ingold, National Research Council Canada, Division of Chemistry, Ottawa, Canada

6.0 Introduction . . . . .	166
6.1 Aminoxy radicals, $RR'\dot{NO}$ . . . . .	167
6.1.1 Bimolecular self-reactions and radical-dimer equilibria . . . . .	167
6.1.1.1 Monoalkylaminoxyls ( $R = \text{alkyl}$ , $R' = \text{H}$ ) . . . . .	167
6.1.1.2 Acyclic dialkylaminoxyls ( $R$ , $R' = \text{alkyl}$ , including $CF_3$ ) . . . . .	167
6.1.1.3 Cyclic aminoxyls ( $R$ , $R'$ , and N form a ring) . . . . .	171
6.1.1.4 Monoarylaminoxyls ( $R = \text{aryl}$ , $R' = \text{H}$ or $e^-$ ) . . . . .	175
6.1.1.5 Acyclic alkarylaminooxyls ( $R = \text{alkyl}$ , $R' = \text{aryl}$ ) . . . . .	176

6.1.1.6 Acyclic diarylaminoxyls (R, R'=aryl) . . . . .	177
6.1.1.7 Acyclic acylaminoxyls (R=acyl, R'=alkyl or aryl) . . . . .	178
6.1.1.8 Nitroaryl radical anions (R=O <sup>-</sup> , R'=aryl), hydroxyarylaminoxyls (R=OH, R'=aryl), and related species . . . . .	180
6.1.2 Reactions with a different radical . . . . .	181
6.1.2.1 Acyclic dialkylaminoxyls (R, R'=alkyl) . . . . .	181
6.1.2.1.1 With carbon-centered radicals . . . . .	181
6.1.2.1.2 With heteroatom-centered radicals . . . . .	182
6.1.2.2 Cyclic aminoxyls (R, R', and N form a ring) . . . . .	182
6.1.2.2.1 With carbon-centered radicals . . . . .	182
6.1.2.2.2 With organic radical ions or zwitterions . . . . .	191
6.1.2.2.3 With solvated electrons (e <sub>aq</sub> <sup>-</sup> ) . . . . .	196
6.1.2.2.4 With hydrogen atoms . . . . .	197
6.1.2.2.5 With hydroxyl radicals or O <sup>·-</sup> . . . . .	198
6.1.2.2.6 With inorganic radical anions . . . . .	198
6.1.2.3 Acyclic alkarylaminoxyls (R=alkyl, R'=aryl); with carbon-centered radicals . . . . .	199
6.1.2.4 Acyclic diarylaminoxyls (R, R'=aryl) . . . . .	200
6.1.2.4.1 With carbon-centered radicals . . . . .	200
6.1.2.4.2 With heteroatom-centered radicals . . . . .	200
6.1.3 Unimolecular reactions . . . . .	201
6.1.3.1 Acyclic dialkylaminoxyls (R, R'=alkyl) . . . . .	201
6.1.3.2 Cyclic aminoxyls (R, R' and N form a ring) . . . . .	202
6.1.3.3 Acyclic acylaminoxyls (R=aryl, R'=alkyl or aryl) . . . . .	204
6.1.3.4 Acyclic alkoxyalkaminoxyls and alkoxyarylaminoxyls (R=alkoxy or siloxy, R'=alkyl or aryl) . . . . .	205
6.1.3.5 Nitroaryl radical anions (R=O <sup>-</sup> , R'=aryl) and hydroxyarylaminoxyls (R=OH, R'=aryl) . . . . .	206
6.1.4 Intermolecular hydrogen atom abstractions from carbon . . . . .	216
6.1.4.1 Acyclic dialkylaminoxyls (R, R'=alkyl) . . . . .	216
6.1.4.2 Cyclic aminoxyls (R, R', and N form a ring) . . . . .	218
6.1.4.3 Acyclic diarylaminoxyls (R, R'=aryl) . . . . .	220
6.1.4.4 Acyclic aroylaminoxyls (R=aroyl, R'=alkyl or aryl) . . . . .	221
6.1.5 Intermolecular hydrogen atom abstractions from oxygen . . . . .	222
6.1.5.1 Acyclic dialkylaminoxyls (R, R'=alkyl) . . . . .	222
6.1.5.2 Cyclic aminoxyls (R, R', and N form a ring) . . . . .	223
6.1.5.3 Acyclic alkarylaminoxyls (R=alkyl, R'=aryl) . . . . .	226
6.1.5.4 Acyclic diarylaminoxyls (R, R'=aryl) . . . . .	227
6.1.6 Intermolecular hydrogen atom abstractions from nitrogen; cyclic aminoxyls (R, R', and N form a ring) . . . . .	228
6.1.7 Intermolecular reactions with molecules in excited states . . . . .	231
6.1.7.1 Acyclic dialkylaminoxyls (R, R'=alkyl) . . . . .	231
6.1.7.2 Cyclic aminoxyls (R, R', and N form a ring) . . . . .	236
6.1.7.3 Aminoxy biradicals . . . . .	246
6.1.8 Other intermolecular reactions . . . . .	249
6.1.8.1 Acyclic dialkylaminoxyl (R, R'=alkyl) . . . . .	249
6.1.8.2 Cyclic aminoxyls (R, R', and N form a ring) . . . . .	251
6.1.8.3 Nitroaryl radical anions (R=O <sup>-</sup> , R'=aryl) . . . . .	252
6.2 Iminoxy radicals, RR'C=NO . . . . .	257
6.2.1 Bimolecular self-reactions . . . . .	257
6.2.1.1 Acyclic dialkyliminoxyls (R, R'=alkyl) . . . . .	257
6.2.1.2 Cyclic iminoxyls (R, R', and C form a ring) . . . . .	258
6.2.1.3 Monoaryliminoxy (R=aryl, R'H) . . . . .	258
6.2.1.4 Acyclic alkaryliminoxyls (R=alkyl, R'=aryl) . . . . .	258
6.2.1.5 Acyclic diaryliminoxyls (R, R'=aryl) . . . . .	259
6.2.2 Unimolecular reactions . . . . .	260
6.2.2.1 Monoalkyliminoxy (R=alkyl, R'=H) . . . . .	260
6.2.2.2 Acyclic dialkyliminoxyls (R, R'=alkyl) . . . . .	260
6.2.2.3 Cyclic iminoxyls (R, R', and C form a ring) . . . . .	262
6.2.2.4 Acyclic alkaryliminoxy (R=alkyl, R'=aryl) . . . . .	263

6.2.3 Intermolecular hydrogen atom abstractions from carbon . . . . .	263
6.2.4 Intermolecular hydrogen atom abstractions from oxygen . . . . .	264
6.2.5 Intermolecular hydrogen atom abstractions from nitrogen . . . . .	264
6.2.6 Other intermolecular reactions . . . . .	265
6.3 Aminothiyl radicals, RR <sup>1</sup> NS <sup>·</sup> , iminothiyl radicals, RR'C=NS <sup>·</sup> , and related species . . . . .	265
6.3.1 Bimolecular self-reactions and radical-dimer equilibria . . . . .	265
6.3.1.1 Acyclic dialkylaminothiyls (R, R'=alkyl) . . . . .	265
6.3.1.2 Cyclic aminothiyls (R, R', and N form a ring) . . . . .	266
6.3.1.3 Iminothiyl radicals . . . . .	267
6.3.1.4 Other radicals . . . . .	267
References for 6.1···6.3 . . . . .	267

## 7 Radicals centered on sulfur, phosphorus and other heteroatoms

B. P. Roberts, Department of Chemistry, University College London, U.K.

7.0 Introduction . . . . .	271
7.0.1 Arrangement of tables . . . . .	271
7.0.2 Definitions . . . . .	271
7.0.3 Coverage . . . . .	271
7.1 Boron-centered radicals . . . . .	272
7.2 Silicon-centered radicals . . . . .	272
7.2.1 Absolute rate constants . . . . .	272
7.2.1.1 Radical-radical reactions . . . . .	272
7.2.1.2 Radical-molecule reactions . . . . .	273
7.2.2 Relative rate constants, radical-molecule reactions . . . . .	281
7.3 Phosphorus-centered radicals . . . . .	287
7.3.1 Absolute rate constants . . . . .	287
7.3.1.1 Rearrangement . . . . .	287
7.3.1.2 Fragmentation . . . . .	295
7.3.1.3 Radical-radical reactions . . . . .	301
7.3.1.4 Radical-molecule reactions . . . . .	302
7.3.2 Relative rate constants, fragmentation or rearrangement . . . . .	304
7.4 Sulfur-centered radicals . . . . .	308
7.4.1 Absolute rate constants . . . . .	308
7.4.1.1 Fragmentation or rearrangement . . . . .	308
7.4.1.2 Radical-radical reactions . . . . .	310
7.4.1.3 Radical-molecule reactions . . . . .	313
7.4.2 Relative rate constants, radical-radical reactions . . . . .	320
7.5 Germanium-centered radicals . . . . .	321
7.5.1 Absolute rate constants . . . . .	321
7.5.1.1 Radical-radical reactions . . . . .	321
7.5.1.2 Radical-molecule reactions . . . . .	322
7.5.2 Relative rate constants, radical-molecule reactions . . . . .	322
7.6 Arsenic-centered radicals . . . . .	322
7.7 Tin-centered radicals . . . . .	323
7.7.1 Absolute rate constants . . . . .	323
7.7.1.1 Radical-radical reactions . . . . .	323
7.7.1.2 Radical-molecule reactions . . . . .	323
7.7.2 Relative rate constants, radical-molecule reactions . . . . .	324
7.8 Mercury-centered radicals . . . . .	337
7.8.1 Absolute rate constants . . . . .	337
7.8.1.1 Radical-radical reaction . . . . .	337
7.8.1.2 Radical-molecule reaction . . . . .	337
References for 7.1···7.8 . . . . .	338