



# Table of contents

## Radical reaction rates in liquids Subvolume a: Carbon-centered radicals I

### General Introduction (H. Fischer)

A Definition and coverage . . . . .	X
B Arrangement and contents of tables . . . . .	X
C Important monographs, series, compilations . . . . .	XII
D Symbols and abbreviations . . . . .	XII

### 1 Carbon-centered radicals: Radical-radical reactions (R.F.C. Claridge)

1.0      Introduction . . . . .	1
1.1      Self reactions . . . . .	2
1.1.1 Primary alkyl radicals . . . . .	2
1.1.2 Secondary alkyl radicals . . . . .	6
1.1.3 Tertiary alkyl radicals . . . . .	11
1.1.4 Cyclo alkyl radicals . . . . .	19
1.1.5 Acyl radicals . . . . .	21
1.1.6 Imidoyl radicals . . . . .	22
1.1.7 Radicals with 3 conjugated electrons . . . . .	22
1.1.8 Radicals with 5 conjugated electrons . . . . .	24
1.1.9 Radicals with 7 conjugated radicals . . . . .	30
1.1.10 Radicals with 9 conjugated electrons . . . . .	40
1.1.11 Radicals with 11 conjugated electrons . . . . .	40
1.1.12 Radicals with 13 conjugated electrons . . . . .	41
1.1.13 Radicals with 15 conjugated electrons . . . . .	48
1.1.14 Radicals with 23 conjugated electrons . . . . .	49
1.1.15 Polymer radicals . . . . .	49
1.2      Cross reactions: Two carbon-centered radicals . . . . .	51
1.2.1 A primary radical with a secondary radical . . . . .	51
1.2.2 Two tertiary radicals . . . . .	51
1.2.3 A tertiary radical with a radical with 7 conjugated electrons . . . . .	53
1.2.4 A tertiary radical with a radical with 13 conjugated electrons . . . . .	53
1.2.5 Two radicals with 7 conjugated electrons . . . . .	54
1.2.6 A radical with 7 conjugated electrons with a radical with 13 conjugated electrons . . . . .	55
1.3      Cross reactions: One carbon-centered radical and a heteroatom-centered radical . . . . .	56
1.3.1 Primary alkyl radicals . . . . .	56
1.3.2 Secondary alkyl radicals . . . . .	59
1.3.3 Tertiary alkyl radicals . . . . .	60
1.3.4 Cyclic alkyl radicals . . . . .	61
1.3.5 Acyl radicals . . . . .	62
1.3.6 Radicals with 7 conjugated electrons . . . . .	63

---

1.3.7	Radicals with 11 conjugated electrons . . . . .	64
1.3.8	Radicals with 13 conjugated electrons . . . . .	64
1.3.9	Radicals with 19 conjugated electrons . . . . .	75
	References for 1 . . . . .	76

**2 Carbon-centered radicals: Radical-molecule addition (E. Roduner, R. Crockett)**

2.0	Introduction . . . . .	79
2.1	Primary alkyl radicals, $\text{R}\dot{\text{C}}\text{H}_2$ . . . . .	80
2.2	Noncyclic secondary alkyl radicals, $\text{R}_1\text{R}_2\dot{\text{C}}\text{H}$ . . . . .	97
2.3	Noncyclic tertiary alkyl radicals, $\text{R}_1\text{R}_2\text{R}_3\dot{\text{C}}$ . . . . .	111
2.4	Cyclic and bicyclic radicals . . . . .	141
2.5	Benzyl radicals . . . . .	155
2.6	Vinyl, acyl and phenyl radicals . . . . .	158
	References for 2 . . . . .	169

**3 Carbon-centered radicals: Fragmentation and rearrangement reactions**

(A.L.J. Beckwith, S. Brumby)

3.0	Introduction . . . . .	171
3.1	Fragmentation reactions . . . . .	172
3.1.1	Carbon-carbon bond fission . . . . .	172
3.1.2	Carbon-heteroatom bond fission . . . . .	175
3.1.3	Concerted ring closure and bond fission . . . . .	180
3.1.4	Other fragmentations . . . . .	181
3.2	Rearrangement reactions . . . . .	182
3.2.1	Aryl migration . . . . .	182
3.2.2	Vinyl migration . . . . .	183
3.2.3	Hydrogen-atom migration . . . . .	184
3.2.4	Heteroatom migration . . . . .	190
3.2.5	Other migrations . . . . .	194
3.2.6	Ring closure . . . . .	195
3.2.6.1	Butenyl and related radicals . . . . .	195
3.2.6.2	Pentenyl and related radicals . . . . .	196
3.2.6.3	Hexenyl and related radicals . . . . .	197
3.2.6.4	Radicals related to heptenyl and higher homologs . . . . .	211
3.2.6.5	Allenyl and related radicals . . . . .	214
3.2.7	Ring opening . . . . .	214
3.2.7.1	Three-membered rings . . . . .	214

---

3.2.7.2	Four-membered rings . . . . .	224
3.2.7.3	Five-membered rings . . . . .	228
3.2.7.4	Six-membered and higher rings . . . . .	230
3.2.7.5	Other ring openings . . . . .	231
3.2.8	Ring expansion . . . . .	232
3.2.8.1	Five-membered rings . . . . .	232
3.3	Conformational change . . . . .	234
3.4	Configurational change . . . . .	246
3.5	Valence bond tautomerism . . . . .	253
	References for 3 . . . . .	254