

CHAPTER 3

Radical Reactions: Part 1

A. J. CLARK and J. SHERRINGHAM

Department of Chemistry, University of Warwick

Introduction	118
Rearrangements	118
Group Migration	118
β -Scission (Ring Opening)	120
Ring Expansion	122
Intramolecular Addition	122
Cyclization	122
Tandem Reactions	128
Radical Annulation	128
Fragmentation, Recombination, and Homolysis	129
Atom Abstraction Reactions	130
Hydrogen Abstraction by Carbon-centred Radicals	130
Hydrogen Abstraction by Heteroatom-centred Radicals	131
Halogen Abstraction	133
Halogenation	134
Addition Reactions	135
Addition to Carbon–Carbon Multiple Bonds	135
Addition to Oxygen-containing Multiple Bonds	137
Addition to Nitrogen-containing Multiple Bonds	138
Homolytic Substitution	138
Aromatic Substitution	138
S_H2 and Related Reactions	138
Reactivity Effects	139
Polarity and Philicity	139
Stability of Radicals	139
Stereoselectivity in Radical Reactions	139
Stereoselectivity in Cyclization	139
Stereoselectivity in Addition Reactions	140
Stereoselectivity in Atom Transfer	141
Redox Reactions	143
Radical Ions	144
Anion Radicals	144
Cation Radicals	144
Peroxides, Peroxyl, and Hydroxyl Radicals	144
Peroxides	144
Peroxyl Radicals	145
Hydroxyl Radical	146
References	147

Introduction

Free-radical chemistry continues to be a focus for research, a number of reviews being published in 1998. In particular, mechanistic considerations have attracted significant interest, with an increasing number of theoretical papers appearing. These theoretical papers have dealt with all aspects of radical chemistry, including the modelling of mechanisms and kinetics of radical processes ranging from biologically relevant radical reactions to those of importance in the atmosphere and in combustion.

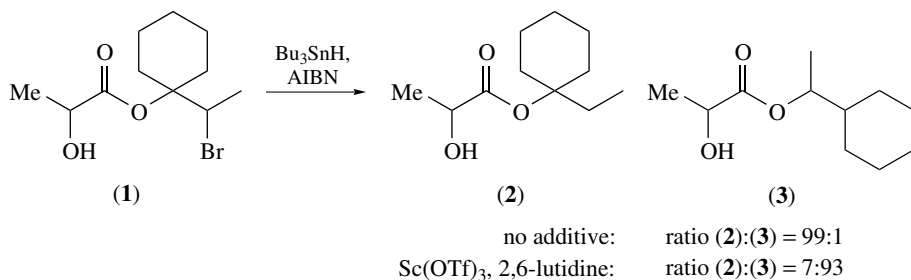
At least 10 reviews on peroxy radicals and their reactions have appeared, ranging in subject from their reactions in the gas phase and in the atmosphere to their ESR spectra and rate constants for formation¹⁻¹⁰ (for more details of these papers, see the *Peroxy Radicals* section of this chapter). The chemistry of aromatic systems has also attracted attention. Comparative quantitative structure–activity relationships (QSAR) for the reactions of a range of radicals with aromatic compounds have been reported.¹¹ This review includes reactions relevant to biological and atmospheric systems as well as conventional organic chemistry. Both the electron-transfer (ET) mechanisms for nitration of aromatics by $\cdot\text{NO}_2$, and $\cdot\text{NO}_3$ as well as the radical-coupling reactions between phenoxy radicals and nitrogen dioxide have also been reviewed.^{12,13} Radical and radical-ionic migrations and fragmentation reactions have been reviewed. The discussion concentrates in particular upon the reactions of β -(acyloxy)alkyl and β -(phosphatoxy)alkyl radicals.¹⁴ In addition, another paper comparing the reactivity of a range of radicals and radical cations has appeared.¹⁵

Turning to the application of radical chemistry in organic synthesis, a review dealing with the cyclization of carbon radicals on to unsaturated CN bonds and the cyclization of a range of nitrogen-centred radicals has appeared.¹⁶ In addition, new synthetic methods utilizing photo-induced single-electron transfer¹⁷ and all aspects of the solution structure, reactivity, and chemistry of carbon-centred fluorine-containing free radicals have been reviewed.¹⁸ The development of asymmetric radical reactions continues with a review appearing on stereoselectivity of hydrogen- and allyl-transfer reactions in acyclic systems.¹⁹ Homolytic substitution reactions have also been reviewed.²⁰

Rearrangements

Group Migration

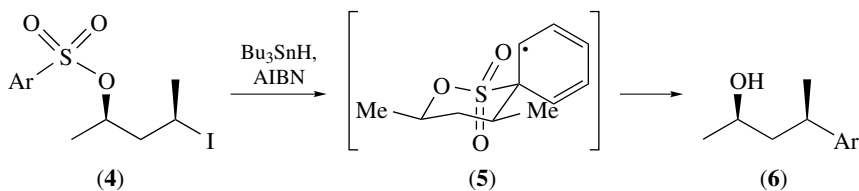
The chemistry and rearrangement reactions of β -(acyloxy)alkyl and β -(phosphatoxy)alkyl radicals have been reviewed.¹⁴ The review incorporates both rearrangement and fragmentation reactions as well as addressing mechanistic considerations. It also addresses QSAR, ESR, and computational aspects of this class of reaction. Rate enhancements of acyloxy rearrangements (**1**) to (**3**) have been observed if the reactions are carried out in the presence of a stoichiometric quantities of Lewis acid (Scheme 1).²¹ Based upon recent calculations, it was postulated that this acceleration upon complexation was due to favouring of the three-electron three-centred shift mechanism for rearrangement. The 1,5-migration of aryl groups from



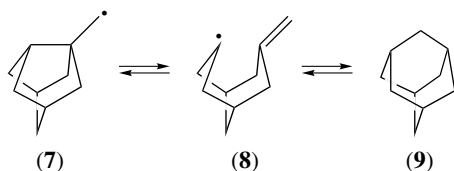
SCHEME 1

sulfur [in a range of arylsulfonates, e.g. (4)] to carbon have been investigated.²² In particular, the stereochemical outcome of these migrations has been studied. Reaction of (4) with Bu₃SnH under standard conditions gave (6) in 76% yield as a 13:1 mixture of diastereomers (Scheme 2). Effective 1,2-stereochemical induction was also observed in the reactions. The observations were explained due to the chair-like transition state arising from *ipso* cyclization via the cyclohexadienyl radical (5).

The chemical vapour disposition (CVD) of diamond is an important process but little information is available on the mechanistic reactions taking place at the surface.²³ Both chemical trapping studies, as well as calculations on model systems for the surface radicals [interconversion of 3-methylenebicyclo[3.3.1]nonan-7-yl (7), (3-noradamantyl)methyl (8), and 1-adamantyl (9) radicals], have been used to investigate the process in more detail (Scheme 3). The thermal isomerization of homoazulene, which involves a ground-state di- π -methane radical rearrangement, has been studied using semiempirical AM1 methods. The activation energies and geometries of each step in the pathway have been calculated.²⁴



SCHEME 2

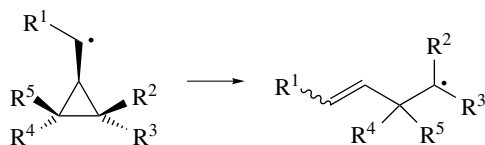


SCHEME 3

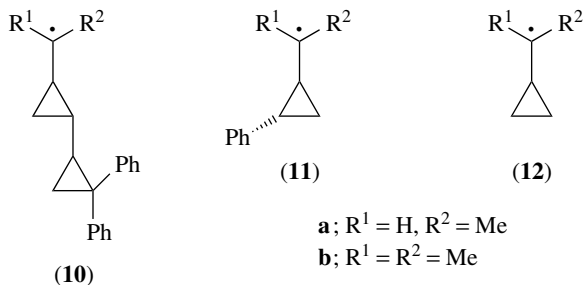
β -Scission (Ring Opening)

Newcomb and co-workers have explored the ring opening of variously-substituted cyclopropylcarbinyl radicals.^{25–27} The electronic effects on the kinetics of cyclopropylcarbinyl radical ring opening have been probed by *ab initio* methods at a range of levels of theory. Whereas vinyl and methoxy substituents on the ring (R^2, R^3, R^4, R^5 in Scheme 4) reduce the activation barriers due to conjugation and hyperconjugation, respectively, when these substituents are at the radical centre (R^1) they raise the barrier.²⁵ Theoretical calculations were in good agreement with experimental data. In addition, ring openings of cyclopropyl groups containing reporter groups have been measured using laser flash photolysis (LFP) methods.²⁷ Three reporter groups were studied, each of which rearranges on the nanosecond time-scale to give UV-detectable benzylic radicals. Interestingly, alkyl radicals (**10a, b**) displayed no kinetic solvent effect whereas the ester-substituted radicals (**10c, d**) did. High levels of theory have also been used to investigate the ring opening of the related hetero-substituted compounds (Scheme 5).²⁸ It was found that the CBS-RAD procedure gave good agreement with experimental thermochemical data. While hetero substitution at the 1-position had little effect on the rate of ring opening, substitution at the 2-position caused a significant rate enhancement. In related work, the fast ring openings of the secondary and tertiary *trans*-2-phenylcyclopropylcarbinyl radicals (**11**) have been determined to be three orders of magnitude faster than those of the corresponding series (**12**).²⁶

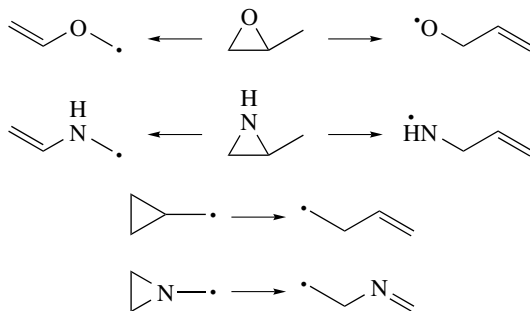
Ring opening of four-membered rings has also been investigated. 2-Oxetanon-4-ylcarbinyl radicals (**13**) undergo a facile ring opening with cleavage of the C–O



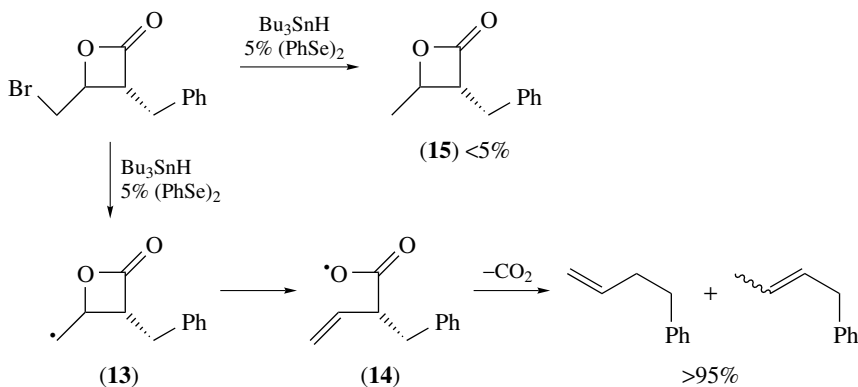
SCHEME 4



- a**; $R^1 = R^2 = H$
b; $R^1 = Me, R^2 = H$
c; $R^1 = CO_2Et, R^2 = H$
d; $R^1 = CO_2Et, R^2 = Me$

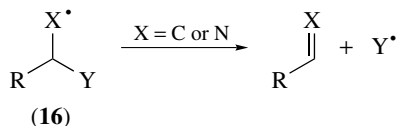


SCHEME 5



SCHEME 6

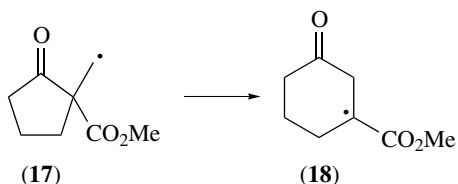
bond to give initially 3-butenoyl radicals (**14**), which, after loss of CO_2 , give allyl radicals. Using conventional $\text{Bu}_3\text{SnH}/\text{AIBN}$ procedures, low yields were obtained owing to poor chain propagation; however, the inclusion of catalytic Ph_2Se_2 gave much cleaner reactions owing to the better H-donor ability of the PhSeH formed *in situ* (Scheme 6). In the presence of a stoichiometric quantity of PhSeH , the reduced product (**15**) was trapped in 80% yield.²⁹ β -Elimination in acyclic systems is also possible. The relative rates of elimination from a number of carbon- and nitrogen-centred radicals (**16**) have been measured. For carbon radicals the order was found to be $\text{Y} = \text{Br} > \text{PhSe} > \text{PhS} > \text{PhSO}_2 > \text{Cl}$, whereas for nitrogen-centred radicals the order $\text{PhSe} > \text{PhSO}_2 > \text{PhS} \approx \text{Br}$ was observed (Scheme 7).³⁰ The effect of solvent upon the rate of β -scission of the *t*-butoxy radical has been determined by LFP.³¹ It was concluded that both the solvent polarity and its ability for hydrogen bonding accelerated the rate of β -scission. The aqueous kinetics of the succinimidyl radical have been examined in the presence of a range of oxidizable substrates and oxygen.³² A rapid equilibrium between the succinimidyl radical and its ring-opened analogue [the β -(isocyanatocarbonyl)ethyl radical] was observed and the equilibrium constant measured.



SCHEME 7

Ring Expansion

The one-carbon ring expansion of (17) to (18) has been accurately measured and proposed as an alternative radical clock to the 5-hexenyl radical to help determine rates in the middle regions of the kinetic scale (Scheme 8).³³ *Ab initio* calculations have indicated that the isomerization of the 3-oxocyclopentylmethyl radical to the 3-oxocyclohexyl radical is energetically more favourable than the process leading to the ring-opened 5-hexenoyl radical.³⁴



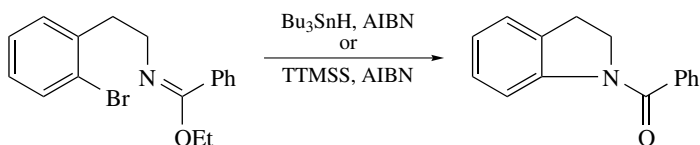
SCHEME 8

Intramolecular Addition

Cyclization

Free-radical cyclization on to unsaturated CN bonds and also the cyclization of a range of nitrogen-centred radicals have continued to attract interest and have been reviewed.¹⁶ Aryl radicals, generated from Bu_3SnH - or TTMSS-mediated homolytic cleavage of aryl-bromide bonds, have been shown to cyclize on to the nitrogen atom of imidate esters in the 5-*exo* mode (Scheme 9).³⁵ Loss of an ethyl radical leads to the observed *N*-acylindolines. No cyclization in the 6-*endo* mode was detected.

Cyclizations of amidyl radicals have been studied both synthetically and kinetically. A detailed study on the rates of a variety of amidyl radical reactions was determined by both LFP and indirect competition methods (Table 1).³⁶ In addition, the rate constants for reactions with Bu_3SnH and PhSH were also reported (thus giving a range of simple amidyl radical clocks). The results obtained will be useful in synthetic sequence-planning involving amidyl radicals.



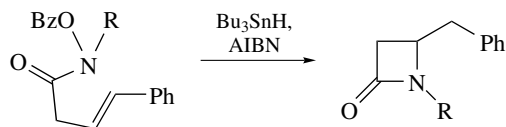
SCHEME 9

TABLE 1

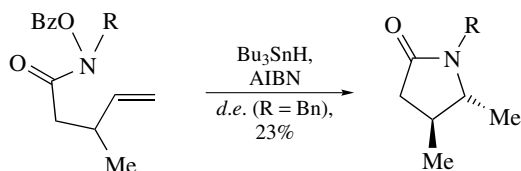
Radical	k_c (s ⁻¹)	k_T (Bu ₃ SnH) (l mol ⁻¹ s ⁻¹)
	2×10^9	1.3×10^9
	5×10^8	1.3×10^9
	1×10^7	1.3×10^9

In synthetic work, amidyl radicals, prepared by Bu₃SnH/AIBN-mediated homolysis of *O*-benzoylhydroxamic acid derivatives, have been shown to cyclize in a 4-*exo* fashion to give β-lactams (Scheme 10).³⁷ In addition, radicals generated in this way have also been reported to undergo 5-*exo* cyclization to give mixtures of *cis*- and *trans*-pyrrolidinones with the steric nature of the *N*-substituent having little effect on the stereochemical outcome (Scheme 11).³⁸ The major products detected were those predicted by application of the ‘Beckwith rule.’

The cyclization of a range of fluorinated radicals has attracted interest.^{39,40} The rate constants for the 5-*exo* cyclization of a range of fluorinated 5-hexenyl radicals have been studied as a function of the position and number of fluorine substituents. For fluorine substituents at or close to the alkene there is little effect on the rate, whereas

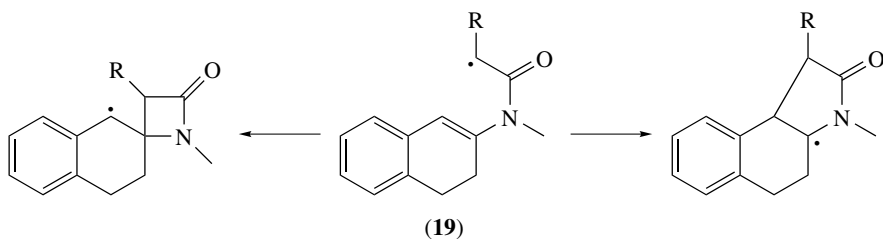


SCHEME 10

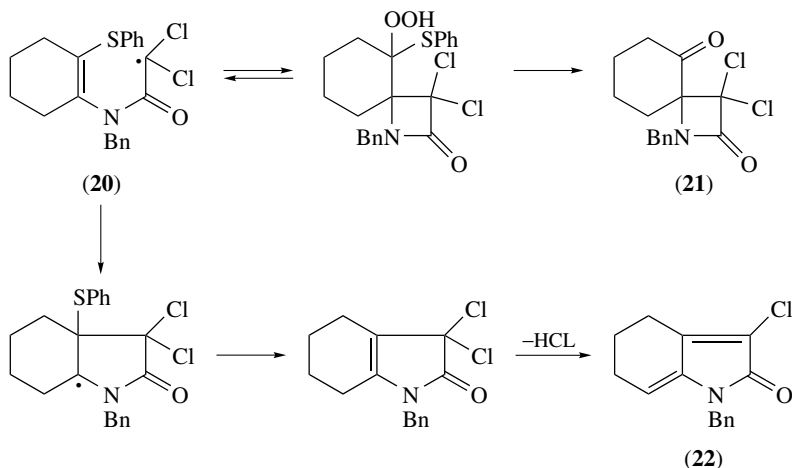


SCHEME 11

fluorine near to the radical centre has a great effect on both the rate and the regioselectivity. These effects were ascribed to both polar and pyrimidalization effects.³⁹ The rate constant for cyclization in the 6-*exo* mode of the 1,1,2,2,3,3,4,4-octafluorohept-6-enyl radical has also been reported and was found to be 3700 times greater than that of the parent hept-6-enyl system. It was also found to be faster than the 5-*exo* cyclization of its fluorinated analogue.⁴⁰ The competition between cyclization in the 4-*exo* and 5-*endo* modes of amide derivatives has been investigated by a number of groups. The effect of the radical substituent R in the Bu₃SnH-mediated cyclization of a range of *N*-vinyl- α -haloamides (**19**) has been reported (Scheme 12).⁴¹ Radical-stabilizing groups (such as Ph and Me) furnish 5-*endo* products, whereas when R = H, the β -lactams are formed. The results were explained based upon the reversibility of the 4-*exo* cyclization leading to the thermodynamic products when R was radical stabilizing. The temperature dependence indicated that lower temperatures favoured the kinetic products. In related work, the cyclization of di- or tri-halo-substituted *N*-vinylamides proceeded to give either 5-*endo* or 4-*exo* products depending on the temperature.⁴² Thus, cyclization of (**20**) at low temperature with Bu₃SnH/Et₃B/O₂ preferentially occurred in a 4-*exo* fashion (kinetic control) to give (**21**) after trapping with O₂; at reflux, however, the 5-*endo* product (**22**) was obtained via an irreversible



SCHEME 12

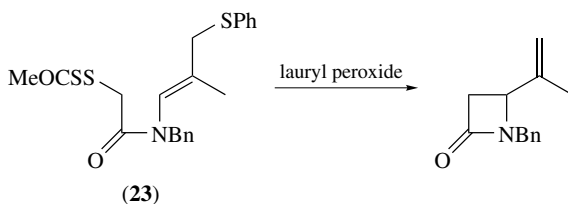


SCHEME 13

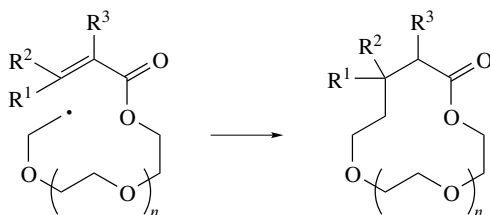
elimination of PhS•. Xanthate derivatives of *N*-ethenylacetamides (**23**) undergo efficient radical cyclization to give β -lactams (Scheme 14).⁴³

Cyclization to give larger ring sizes has been reported to be mediated by Bu₃SnH.⁴⁴ The effects of chain length (12-, 15-, 18-, 21- and 24-membered rings) and the substituents present on the chain on the outcome of the reactions and the effect of solvent were evaluated (Scheme 15). The rate constants determined for cyclization at 80 °C in benzene for a variety of chain lengths were shown to be 10–30 times greater than those for the cyclization of the corresponding parent alkenyl species, presumably owing to the decrease in strain energy in the transition state.

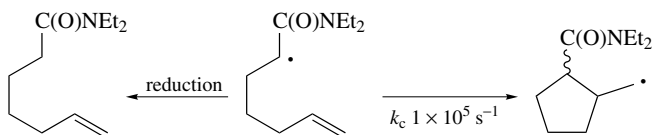
The absolute rate constants for a variety of cyclizations have been measured. In particular, the rates of decarbonylation of a variety of alkoxy-carbonyl radicals have been obtained by LFP studies on PTOC oxalates.⁴⁵ From these data, rate constants for the reduction of alkoxy-carbonyl radicals with Bu₃SnH and their 5-*exo* cyclizations were determined. Whereas cyclizations were slightly faster than the analogous alkyl radical 5-*exo* cyclizations, their reactions with Bu₃SnH were 10 times slower, indicating that cyclization processes should be synthetically useful. The rate constants for the cyclization of a number of variously substituted α -amide radicals have been determined together with their relative reactivities towards reduction using Bu₃SnH (Scheme 16).⁴⁶ Cyclizations of secondary-based radicals were found to be similar to the corresponding alkyl-substituted radicals. In addition, the rate constants were subject to minor electronic



SCHEME 14



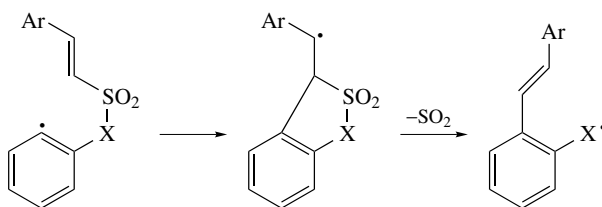
SCHEME 15



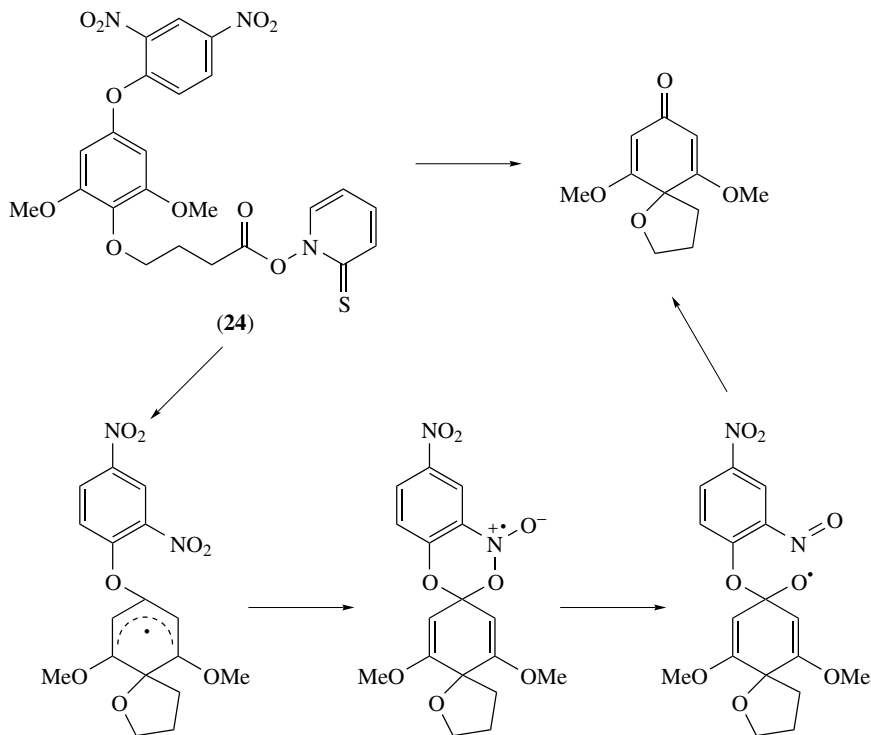
SCHEME 16

effects (as in the case of α -ester radicals) but steric effects led to reductions in rates far greater than those observed in other electron-deficient radical cyclizations.

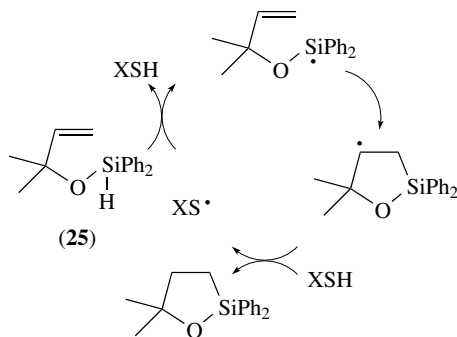
A model radical-reaction system has been used to probe the postulated radical rearrangement/cyclization mechanism proposed for the growth of diamond by chemical vapour deposition.²³ The results of these model studies agree with low-level calculations used to model a large section of the diamond surface. Unsymmetrical stilbene derivatives have been prepared by 5-*exo* cyclization of aryl radicals on to vinyl sulfonamides and sulfonates followed by elimination of SO₂ (Scheme 17).⁴⁷ The mechanism of the spiro-cyclization of (**24**) has been investigated. On the basis of isotopic labelling studies, it was proposed that oxygen transfer from an NO₂ group to a cyclohexadienyl radical was the most likely process (Scheme 18).⁴⁸



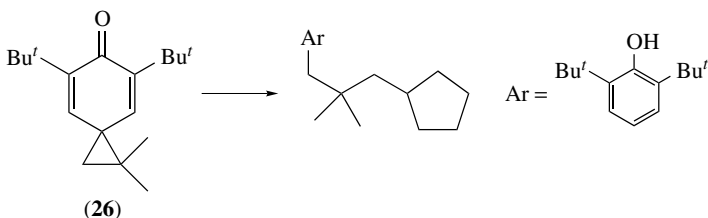
SCHEME 17



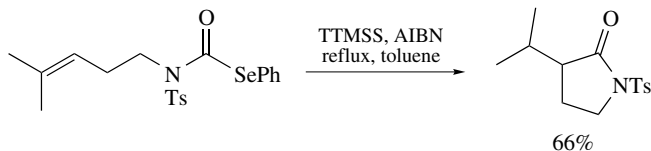
SCHEME 18



SCHEME 19



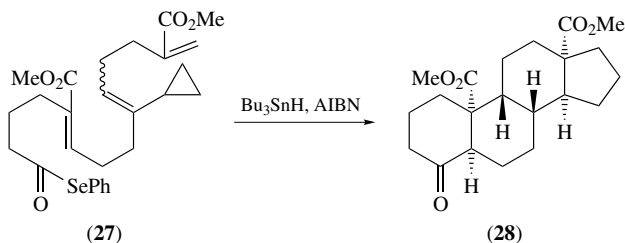
SCHEME 20



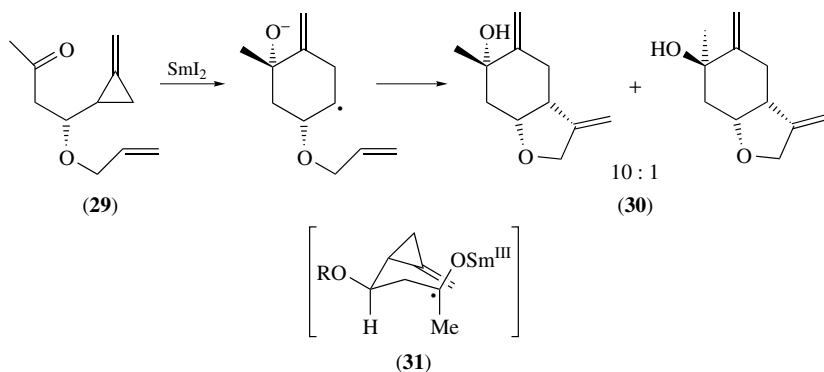
SCHEME 21

Radical-chain cyclization of alkenyloxysilanes using thiol catalysts give five-membered ring products (via a 5-*endo* cyclization) in the case of allyloxysilanes (25) (Scheme 19).⁴⁹ Homoallyloxysilanes gave a mixture of five- and six-membered rings, but the intermediate silyl radical underwent predominantly 6-*endo* cyclization. Pentyloxysilane gave the 7-*endo* product only. The stereochemistry of these reactions was found to be determined by steric effects, even in the presence of chiral thiol catalysts. The structures of the radical intermediates were studied by EPR.

The radical-ion probe (26) has been used mechanistically to investigate the addition of Grignard reagents to conjugated carbonyl compounds (Scheme 20).⁵⁰ Reaction of (26) with 5-hexenylmagnesium bromide indicated that cyclization occurred mainly by a polar process; however, the detection of products arising from reaction via a cyclopentylcarbinyl rearrangement indicated freely diffusing paramagnetic intermediates. Carbamoyl radicals derived from *Se*-phenyl selenocarbamates undergo efficient intramolecular addition to alkenes (Scheme 21).⁵¹ Substituent effects for the regioselectivity of cyclization of vinyl radicals on to aromatic rings have been reported.⁵²



SCHEME 22



SCHEME 23

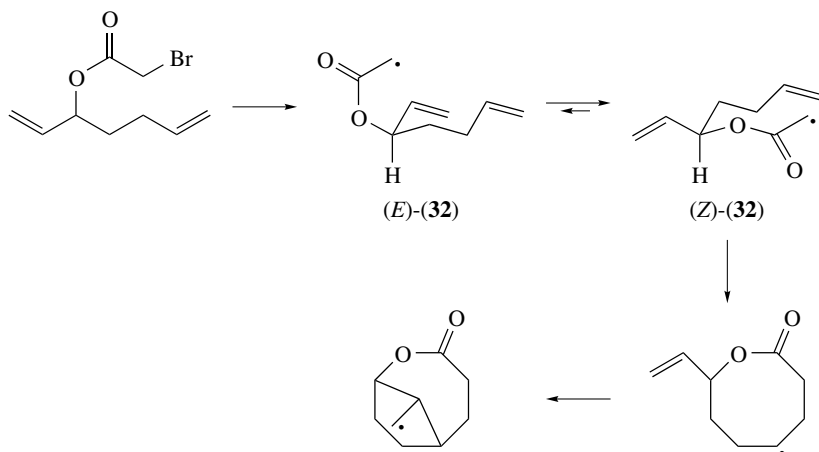
Tandem Reactions

The ability to sequence radical reactions continues to be a great advantage in the use of radical chemistry in synthesis. For example, the controlled sequencing of five different reactions leads to the formation of the steroidal skeleton **(28)**.⁵³ Thus, two 6-*endo* cyclizations followed by a cyclopropyl ring opening/9-*endo*-trig/transannular cyclization furnishes **(28)** from **(27)** in 45% yield (Scheme 22). The ring opening of cyclopropyl radicals has also been utilized in a cascade process leading to bicyclic systems.⁵⁴ Thus, SmI₂-mediated reaction of the methyl 2-cyclopropylethyl ketone (**(29)**) to give ethers (**(30)**) proceeds with high stereoselectivity (Scheme 23). The stereoselectivity was dependent on the presence of additives (HMPA, 10:1 mixture, DMPU 1.5:1, no additive 1:1.3). Cyclization via the transition state **(31)** was postulated to explain the stereoselectivity.

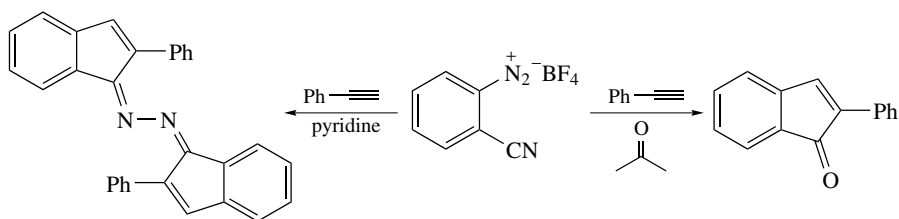
The tandem 8-*endo*/5-*exo* cyclization of the (alkoxycarbonyl)methyl radical (**(32)**) has indicated that 8-*endo* cyclization is favoured over 5-*exo* cyclization in this system (Scheme 24).⁵⁵ *Ab initio* studies indicated that this was due to the initial radical favouring a (*Z*)-(**(32)**) over an (*E*)-(**(32)**) conformation.

Radical Annulation

A novel [3 + 2] radical annulation of *o*-cyano-substituted aryl radicals with alkynes has been reported.⁵⁶ The reactions occur by addition of the aryl radical to the alkynes



SCHEME 24



SCHEME 25

followed by cyclization of the resulting vinyl radical on to the cyano group to give an imine radical. The fate of this radical is then determined by the reaction conditions (Scheme 25).

Fragmentation, Recombination, and Homolysis

Radical-recombination reactions play an important role in combustion and atmospheric processes. Reactions that have no energy barrier along the reaction coordinate have become increasingly studied theoretically. For example, canonical flexible transition-state theory (CFTST) has been used to determine the temperature dependences of the self-recombination of Me^\bullet , $\text{F}_3\text{C}^\bullet$ and $\text{Cl}_3\text{C}^\bullet$ radicals.⁵⁷ There was found to be good agreement between theoretical data and experiment. Both the combination reactions of Me^\bullet with ethane and of Me^\bullet and H^\bullet with methane have been examined theoretically at high temperatures and pressures.^{58,59} For both processes the combination was best described by the formation of a weakly-bound intermediate with the contribution of a strongly bound complex for the Me^\bullet recombination being one order of magnitude smaller. For the $\text{CH}_3 \cdots \text{H}$ complex, the contribution involving a strongly bound complex was dependent on temperature. The recombination of peroxy radicals in the gas phase has been reviewed.² The review concentrates on both kinetic and mechanistic

aspects. Key reactions that underpin new non-bromine-containing fire-extinguishing methods have been studied theoretically (MP2, QCISD, B3LYP, GAUSSIAN-1 and -2).⁶⁰ In particular, the reactions between $\cdot\text{CF}_3$ and both $\text{HO}\cdot$ and $\text{H}\cdot$ have been probed. The recombination reactions of methyl radicals ($\cdot\text{CH}_3$, $\cdot\text{CH}_2\text{D}$ and $\cdot\text{CHD}_2$) with $\text{D}\cdot$ have been studied at low pressures.⁶¹ At 1 Torr the initially formed methane complex was found not to be stabilized.

Ab initio methods have been used to locate the potential-energy surface and transition states for a series of hydrogenolysis reactions in order to determine whether the Marcus equation could be extended to atom-transfer reactions.⁶² It was concluded that there was not good agreement with the Marcus equation owing to the latter's neglect of Pauli repulsion. If the Pauli repulsion terms were considered, then an equation that fits the data can be constructed. This indicated that the repulsions were important and should be considered in atom-transfer or ligand-transfer reactions. The homolytic bond-dissociation enthalpies of the C–H bonds adjacent to a variety of hydrocarbon, allylic and benzylic radicals have been calculated using the *ab initio* CBS-4 method.⁶³ Calculations suggested that radical centres typically weaken the neighbouring C–H bond strength by about 50–70 kcal mol⁻¹. In other theoretical work the thermochemistry of the reactions between $\text{HSCH}_2\cdot$ and O_2 , NO , and NO_2 have been calculated by HF, MP2, DFT, CBS-4, CBS-Q and G2MP2 methods.⁶⁴

Hydrogen abstraction from propan-2-ol and propan-2-ol-*d*₇ by hydrogen and deuterium atoms has been studied by pulsed radiolysis FT-ESR.⁶⁵ A secondary kinetic isotope effect was observed for $\text{H}\cdot$ ($\text{D}\cdot$) abstraction from the C–H (C–D) bonds. The results were compared with *ab initio* data. In similar work, the kinetic isotope effects in $\text{H}\cdot$ and $\text{D}\cdot$ abstraction from a variety of other alcohols in aqueous solvents have been measured.⁶⁶ It was found that, compared with the gas phase, the reactions exhibit higher activation energies in agreement with the ability of solvation to decrease the dipole moment from the reactant alcohol to the transition state.

The pressure dependence of the reaction between butane-1-thiol and hydrogen atoms at 133, 266, 532, 2660, and 5320 Pa, using two types of fast-flow discharge reactors, have been studied.⁶⁷ Butane and but-1-ene were the main products. Pressure dependence indicated decomposition through vibrationally activated species.

Bromine-atom atomic resonance absorption spectrometry (ARAS) has been applied to measure the thermal decomposition rate constants of CF_3Br in Kr over the temperature range 1222–1624 K.⁶⁸ The results were found to be consistent with recently published theory. The formation of cyclopent[*a*]indene and acenaphthylene from alkyl esters of biphenyl-mono- and -di-carboxylic acids has been observed in flash vacuum pyrolyses at 1000–1100 °C.⁶⁹ The kinetics and mechanisms of free-radical generation in the ternary system containing styrene epoxide, *p*-TsOH, and *i*-PrOH have been examined in both the presence and absence of O_2 .⁷⁰

Atom Abstraction Reactions

Hydrogen Abstraction by Carbon-centred Radicals

Hydrogen abstraction by fluorinated and chlorinated radicals has attracted a good deal of attention.^{71–73} The rates of H-abstraction by both the perfluoroisopropyl and *t*-butyl

radicals have been measured and compared with those for non-fluorinated analogues.⁷¹ The rate constants of 3.6×10^6 and $2.4 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ were much higher than for their respective non-fluorinated analogues. In the case of $t\text{-C}_4\text{F}_9^\bullet$ it was found to be more reactive than the highly electrophilic $(\text{Me})_3\text{CO}^\bullet$ radical. The kinetics of hydrogen abstraction by the $\text{CF}_3\text{CO}-\text{C}(\text{C}_2\text{F}_5)_2$ radical have been studied by ESR and a reaction mechanism proposed.⁷² Hydrogen abstraction from a range of cycloalkanols by $\text{Cl}_3\text{C}^\bullet$ has been studied.⁷³ The authors proposed that under specific conditions the reactivity of the C–H bonds is controlled by hyperconjugation of neighbouring C–H bonds, rather than I-strain or radical stability.

In theoretical work, the initial steps in the polymerization of 1,1-dicyano-, 1,1-difluoro-, and 1,1-dimethyl-cyclopropanes by reaction with H^\bullet , $\bullet\text{OH}$, and Me^\bullet have been modelled by *ab initio* methods.⁷⁴ Other *ab initio* MO calculations for the reactions of H^\bullet , Me^\bullet , Et^\bullet , $i\text{-Pr}^\bullet$, and $t\text{-Bu}^\bullet$ with a variety of silanes and germanes have been carried out.⁷⁵ The results indicate that the attacking and leaving radicals adopt an almost co-linear arrangement. Bond distances and energy barriers were predicted for the reactions studied.

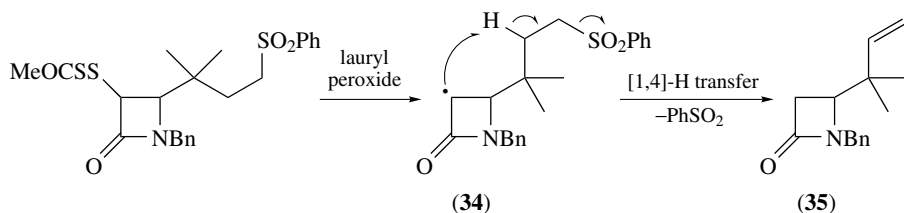
In kinetic studies, the abstraction of F^\bullet from $\text{CF}_3\text{CH}_2\text{OH}$ by $\text{ArN}_2^+\text{BF}_4^-$ was shown to be an ionic process, whereas abstraction of an $\alpha\text{-H}$ atom from $\text{CH}_3\text{CH}_2\text{OH}$ was determined to be a radical process.⁷⁶ In other kinetic work, the expansion of cyclopentanones has been used to measure the kinetics of hydrogen-atom abstraction reactions for a range of hydrogen donors in benzene including $(\text{MeO})_2\text{P}(\text{O})\text{H}$ ($1.2 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$) and $(\text{MeS})_3\text{SiH}$ ($3.9 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$).³³

The feasibility of hydrogen abstraction at the peptidyl $\alpha\text{-carbon}$ hydrogen bond by 1,4-aryl diradicals has been determined by examining a model reaction, i.e. abstraction of deuterium from dideuterioglycine by aryl radicals.⁷⁷ The results have biological implications for the reactivity of the enediyne anti-tumour antibiotics with proteins. The non-Arrhenius behaviour of hydrogen-abstraction reactions by radicals has been investigated.⁷⁸ For a number of reactions studied the enthalpy of activation was found either to increase or to decrease as a function of temperature.

An example of the relatively rare 1,4-hydrogen-atom transfer has been invoked in the reaction of (34) to give (35); see Scheme 26.⁴³

Hydrogen Abstraction by Heteroatom-centred Radicals

Abstraction reactions in biological systems, in particular the site of radical attack in proteins (oxidative damage), continue to be a matter of great interest, primarily owing



SCHEME 26

to their implicated role in ageing and other disorders. In the light of this interest, *ab initio* studies have been used to calculate bond-dissociation energies and transition states for hydrogen-atom abstraction by thiyl radicals [B3LYP/6-31G(D)] in both cysteine and model peptides.⁷⁹ In addition, implications for the radical-induced strand cleavage of DNA have been examined by observing the racemization of the model tetrahydrofurfuryl acetate under a range of conditions.⁸⁰ Whereas the presence of alkanethiols was ineffective in promoting racemization, those containing electron-withdrawing *S*-alkyl groups (1-thio- β -D-glucopyranose and 2,2,2-trifluoroethanethiol) acted as good promoters of radical racemization via 'polarity reversal catalysis.' The mechanism of 'polarity reversal catalysis' has been probed using a variety of theoretical methods to examine the hydrogen-atom transfer reaction between silane and the methylthiyl radical.⁸¹ At the highest level of theory, CCSD(T)/aug-cc-pVDZ/MP2/aug-cc-pVDZ calculations predict the abstraction to proceed with an energy barrier of 34.0 kJ mol^{-1} while being endothermic by $18.3\text{--}34.0 \text{ kJ mol}^{-1}$. These calculations indicate that sustainable chain reactions are certainly possible by invoking the traditional explanation for the origin of the 'polarity reversal catalysis.'

Hydrogen abstraction by halogens has attracted much study, in particular the abstraction by Cl^\bullet . H-atom abstraction from propane by Cl^\bullet has been studied using VUV synchrotron radiation in a crossed molecular beam.⁸² The rate coefficients for the abstraction of H^\bullet from methane, ethane, propane, and butane by Cl^\bullet have been measured by pulsed-laser photolysis resonance fluorescence.⁸³ The laser flash photolysis fluorescence technique has also been used to investigate the kinetics and mechanism of the reaction between Cl^\bullet and MeI as a function of temperature (218–694 K).⁸⁴ Above 364 K, the rates were found to be independent of pressure and a significant H/D kinetic isotope effect was measured, indicating that hydrogen transfer was the dominant pathway; on the other hand, at temperatures lower than 250 K, rates were pressure dependent; at temperatures between 263 and 309 K reversible addition was observed. In theoretical work, *ab initio* calculations have been performed for reactions involving channel hydrogen abstraction from methanol by Cl^\bullet , Br^\bullet , and F^\bullet .^{85,86} The calculations showed that all three reactions proceed via formation of intermediate complexes. Rate-constant calculations were found to be in good agreement with experimental data.

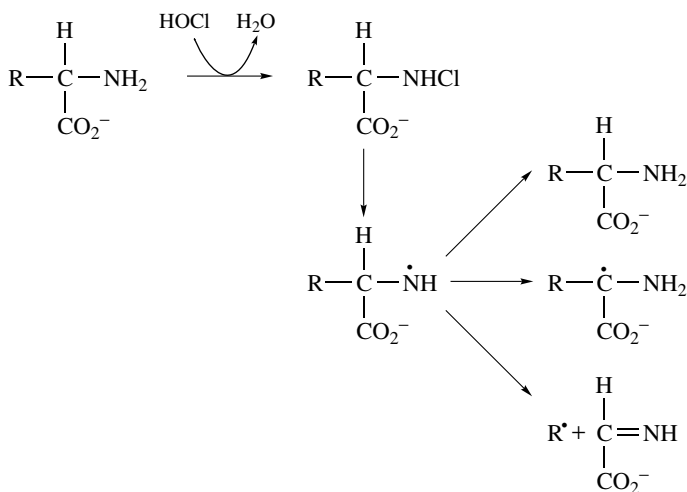
Hydrofluoro ethers have been proposed as a new generation of CFC alternatives. The absolute rate constants for the abstraction of a hydrogen atom by Cl^\bullet with several hydrofluoro ethers have been examined using VLPR monitored by quadrupole MS.⁸⁷ The rate parameters for abstraction were found to correlate well with the theoretical C–H bond strengths determined by *ab initio* calculations.

Reactions mediated by F^\bullet have also been investigated. The absolute rate constants for hydrogen-atom abstraction from CHF_3 , CHClF_2 , CHCl_2F and CHCl_3 by fluorine atoms have been reported.⁸⁸ Using a pulsed-radiolysis UV–vis absorption system, the rate constants for reaction of F^\bullet with MeCHO and of O_2 with MeCO have been measured at 295 K at 1000 mbar.⁸⁹ The two possible H-abstraction reactions of CHF_2CH_3 with F^\bullet atoms were studied through theoretical calculations and were found to be in good agreement with experimental values.⁹⁰ The same authors have also measured the rate constants and kinetic isotope effects (1.4 ± 0.2) for direct hydrogen abstraction

by Cl^\bullet from butane and butane-*d* using both the relative-rate method (GC-FID) and resonance fluorescence (FFDS).⁹¹ Both methods were in good agreement.

Hydrogen-atom abstraction from a range of alkyl-substituted aromatics by peroxy radicals has been examined by statistical analysis based upon MINDO/3 calculations. The role of various structural factors in the regioselectivity of abstraction was examined and discussed.⁹² A range of theoretical methods, ranging from DFT to *ab initio* methods, have been used to examine hydrogen abstraction from ethane by the hydrogen atom and conclusions as to the best systems to employ were discussed.⁹³ Comments upon the Roberts and Steel and Zavitsas methods for calculating energies of activation of hydrogen-atom abstractions have appeared, and the limitations of both approaches highlighted.⁹⁴ The Zavitsas approach has been used to calculate the $\text{H}^{18}\text{O}-\text{H}/\text{HO}^\bullet$ identity reaction in the light of recent experimental results.

The reaction of amino acids with HOCl was studied using EPR spin trapping and UV-vis spectroscopy.⁹⁵ Some nitrogen-centred radicals, which then undergo a variety of abstraction, rearrangement, and fragmentation reactions, were detected (Scheme 27).



SCHEME 27

Halogen Abstraction

Halogen abstraction by $\text{Bu}_3\text{Sn}^\bullet$ has been studied by a number of groups. The activation energies for halogen abstraction from a range of aliphatic, benzylic, and aromatic halides have been measured and the results compared with the bond-dissociation energies of the $\text{C}-\text{X}$ bond.⁹⁶ In addition, the absolute rate constants for the abstraction of bromine from a range of aromatic bromides by $\text{Bu}_3\text{Sn}^\bullet$ has been reported.⁹⁷ For the particularly hindered 2,4,6-tri-*t*-butylbromobenzene, the rate was found to be unusually fast, presumably owing to steric acceleration. *Ab initio* calculations at various levels of theory have been used to investigate the hydrogen-atom transfer of

various ω -halo-1-alkyl radicals. It was found that, for 1,5- to 1,7-halogen transfer, the reaction took place via C_2 or C_s symmetric transition states. No 9-X-2 intermediates were located in the study.⁹⁸ In other theoretical work, halogen abstraction from CF_4 , CF_3Cl , CF_3Br , and CF_3I by Me^* has been studied theoretically at HF/6-31G(d) and MP2 = full/6-31G(d) levels of theory.⁹⁹ Transition states, energy barriers and rate constants were calculated (298–2500 K range). The computed results were accurate to ± 61 kJ mol⁻¹ over the 360–500 K range. Conclusions were drawn with respect to flame-suppression chemistry.

A range of traditional *ab initio* methods (HF, MP2, MP4) have been compared with DFT methods (B3LYP, BLYP) in the Cl-abstraction reactions of $MeCl$, CH_2Cl_2 , and $CHCl_3$ by the silyl (H_3Si^*) and trichlorosilyl (Cl_3Si^*) radicals, respectively.¹⁰⁰ While HF, MP2, and MP4 largely over-estimated the activation barrier, DFT approaches gave results in good agreement with experiment (B3LYP being the best).

The relative importance of bromine-atom abstraction, relative to hydrogen abstraction, in the reactions of C_3H_7Br , C_4H_9Br , *s*- C_3H_7Br , and *s*- C_4H_9Br with the hydrogen atom have been estimated by bond-energy bond-order (BEPO) calculations.¹⁰¹ The rate coefficients for the reactions were determined by experiment in a discharge flow reactor and good agreement with predictive information was achieved. The reaction of thiolate ions with a range of 2,2,2-trifluoroethyl halides under UV irradiation at room temperature has been investigated.¹⁰² These reactions led to the generation of the trifluoroethyl radical (detected by ESR), indicating that the processes were proceeding via an $S_{RN}1$ reaction.

Halogenation

The chlorination of alkanes has been investigated in supercritical CO_2 (SC- CO_2).¹⁰³ The chlorine-atom cage effect was used to probe the effect of viscosity and solvent clusters on reactivity and cage lifetimes. No evidence was found for an enhanced cage effect. Chlorine-atom selectivities were found to be intermediate between the gas and liquid phases. The lower viscosity of SC- CO_2 , compared with conventional solvents, allows absolute rate constants to exceed 10^{10} l mol⁻¹ s⁻¹ and the tuneable solvent properties allow a means of controlling both reactivity and selectivity. The free-radical chlorination of alkanes has also been examined in a range of chlorinated solvents.¹⁰⁴ The results indicate that Cl^* forms a complex with halogenated solvents, with the selectivity of hydrogen abstraction decreasing with increasing Cl content of the solvent (i.e. increasing ionization potential of the solvent).

The mechanism of addition of Cl_2 and Cl^* to both alkynes¹⁰⁵ and alkenes^{106,107} has been reported. Theoretical calculations have shown that the addition of Cl_2 to C_2H_2 proceeds through a free-radical mechanism, the initial step being the generation of Cl^* and $C_2H_2Cl^*$ radicals.¹⁰⁵ In a reply to comments on previously reported work¹⁰⁶ on the inverse kinetic isotope effect observed for the addition of Cl^* to C_2H_4 and C_2D_4 , it was highlighted that, owing to the large standard deviation in the experiment (27%) and limited number of experiments conducted in He, deriving values for the third-body efficiency of N_2 versus He was not appropriate. However, it was also pointed

out that this would not affect the ultimate conclusion that there was an inverse kinetic isotope effect of about 3 for the reactions examined.¹⁰⁷

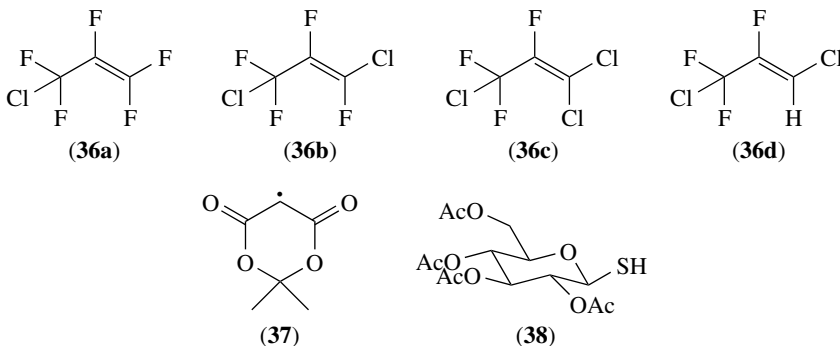
The kinetics of the reactions of photo-generated $\cdot\text{CH}_2\text{Cl}$, $\cdot\text{CHBrCl}$, $\cdot\text{CCl}_3$, and $\text{CH}_3\text{C}\cdot\text{Cl}_2$ radicals with Cl_2 have been measured. In addition, the transition states for the four reactions were localized and optimized at the MP2/6-31G(d,p) level of theory. The kinetics were found to be controlled by the electronic nature of the substituents.¹⁰⁸

Addition Reactions

Addition to Carbon–Carbon Multiple Bonds

The regioselectivity of the addition of nucleophilic radicals, derived from alcohols and ethers, to a range of chlorofluoropropenes (**36a–d**) have indicated that selectivity is dependent on the number of chlorine atoms on the alkene.¹⁰⁹ Thus, addition to (**36c**) proceeds in an anti-Kharash mode while the rates of addition decreased with increasing chlorine substitution. In theoretical work, the regioselectivity of addition of the methyl radical to fluoroethanes has been studied using quantum-mechanical calculations.¹¹⁰ While the Hartree–Fock (B3LYP) method is reliable in calculating activation energies and reaction enthalpies, it fails to predict accurately the regioselectivity of addition. Coupled cluster calculations were found to be far more reliable. Similar calculations on the addition of $\text{Me}\cdot$ to alkenes using DFT methods have shown that, in comparison with $\cdot\text{CH}_2\text{OH}$, $\text{Me}\cdot$ does not behave as a nucleophile.¹¹¹ The addition of other carbon radicals to alkenes has also been investigated by *ab initio* calculations at a variety of levels of theory. Closest agreement with experimental barriers was found with the use of the CBS-RAD procedure.¹¹² In other theoretical work, molecular-orbital calculations have been used to study the addition of a range of free radicals to alkenes.¹¹³ High levels of theory were required to obtain useful data. Polar effects were found to be important for the addition of $\cdot\text{CH}_2\text{OH}$, $\cdot\text{CH}_2\text{CN}$, and $\text{Me}_3\text{C}\cdot$ radicals.

The addition of a range of perfluoro-*n*-alkyl radicals to both $\text{CH}_2=\text{CHCH}_2\text{C}_4\text{F}_9$ and $\text{CH}_2=\text{CHC}_4\text{F}_9$ have been studied and the rate constants determined as 1.15×10^6 and $2.6 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$, respectively, at 298 K.¹¹⁴ The mechanism for the addition of both $\text{Me}\cdot$ and $\cdot\text{CF}_3$ to fluoroethylene has also attracted attention.¹¹⁵ The results



indicated that, regardless of fluoro substitution, the alkenes acted as electron donors whereas the radicals acted as electron acceptors. The anomaly in the regioselectivity found for the addition of both Me^\bullet and $\bullet\text{CF}_3$ radicals to trifluoroethylene was explained in electrostatic terms. The radical addition to a series of cyclopentenones and cyclohexenones was found to occur primarily at the 3-position (kinetic product) at lower temperatures, but at higher temperatures or with a hindered 3-position addition occurred at the oxygen atom.¹¹⁶

The absolute rate constants for the addition of the cyclic malonyl radical (**37**) and the di(*t*-butyl)malonyl radical to over 26 different alkenes have been measured by time-resolved ESR spectroscopy.¹¹⁷ Rate constants range from $1.1 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$ (acrolein) to $2.41 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ (1,1-diphenylethene) with activation energies ranging from 12.9 kJ mol^{-1} (1,1-diphenylethene) to 21.7 kJ mol^{-1} (acrylonitrile). Correlation with alkene ionization potential and reaction enthalpy was observed. No correlation between the activation energy and the alkene electron affinities was found.

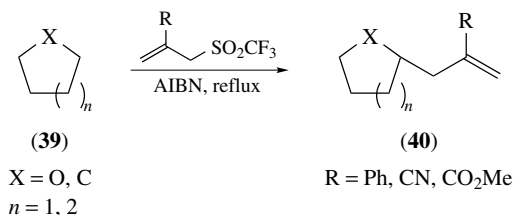
In atmospheric chemistry, reactions between pure nitric oxide and a range of activated alkenes have been examined. However, no addition products were observed.¹¹⁸ Only in the presence of NO_2 was addition to give β -nitroalkyl radicals, followed by trapping to β -nitronitroso compounds, observed. These final products can also trap other radicals to give aminoxyl radicals.

In order to determine the fate of $\bullet\text{NO}_3$ at night in the troposphere, an *ab initio* study on the mechanism of the reaction of $\bullet\text{NO}_3$ with ethene has been reported.¹¹⁹ The theoretical data show that, out of the three possible reaction channels to give oxirane, ethanol, or nitric acid, the formation of oxirane is kinetically favoured at low pressures. In other atmospheric-chemistry studies, there is increasing evidence that suggests that brominated compounds play a significant role in ozone chemistry, and this has prompted interest in studying the low-pressure (0.5–2.0 Torr) reaction between bromine atoms and propene (233–320 K) using mass spectrometric discharge flow methods.¹²⁰ Both the abstraction and addition pathways were observed and Arrhenius expressions obtained.

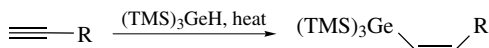
The rate constants for the addition of a range of carbohydrate and *myo*-inositol-based radicals to acrylic acid have been measured using EPR spectroscopy.¹²¹ The addition of α -keto radicals to allylsilanes has been reported and is heavily dependent on the substitution, size, and electronic properties of substituents attached to the silicon atom. Thus, electron-donating groups promote the additions but increased steric demand at silicon retards them.¹²² Radicals derived from α -halo esters in the presence of Ph_3SiH were found to add efficiently to electron-rich alkenes in the presence of thiols as polarity-reversal catalysts.¹²³ The use of optically active thiols such as the glucose derivative (**38**) proceeds to give adducts with induced enantioselectivity. Thiols have also been shown to catalyse the addition of primary aldehydes to terminal alkenes to give ketone adducts in moderate yields.¹²⁴ The hydroacylation reaction was effective for electron-rich, neutral, and electron-deficient alkenes, with the former being the most efficient reactions. Triorganosilanethiols also function as catalysts. The role of the thiol was postulated to be that of a polarity-reversal catalyst which promoted hydrogen-atom transfer from the aldehyde to the carbon-centred radical produced by addition of the acyl radical to the alkene.

The ability to conduct radical reactions without the use of tin reagents is important. Allylic triflones have been used to conduct allylation reactions on a range of substrates (39) as a replacement for allyltributylstannane (Scheme 28).¹²⁵ The main limitation was that unactivated or trisubstituted triflones failed to undergo reactions. In other non-radical methods, arenesulfonyl halides have been used as functional initiators in the CuCl/4, 4'-dinonyl-2, 2'-bipyridine-catalysed 'living' atom-transfer polymerization of styrenes, methacrylates, and acrylates.¹²⁶ The kinetics of initiation and propagation were examined with a range of substituted arylsulfonyl halides with initiator efficiency measured at 100%.

A range of addition reactions of (TMS)₃GeH with alkynes, alkenes, ketones, azines, and quinones has been studied using EPR.¹²⁷ In addition, synthetic ketones of hydrogermylation of alkynes have shown that the reaction proceeds regio- and stereo-selectively, whereas reactions with alkenes do not take place (presumably owing to the reversibility of the germyl radical addition) (Scheme 29).



SCHEME 28

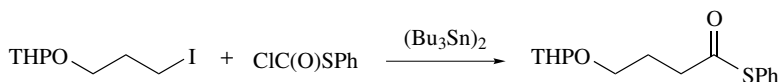


SCHEME 29

The reactions of *N*-phenyl α -*t*-butyl nitron (PBN) with maleimides, maleic anhydride, and diethyl maleate have been studied by EPR and two types of spin adduct detected. They arise from the reductive addition of PBN to the alkenes and the degradation product of DBN (2-methyl-2-nitropropane).¹²⁸ The deuterium and muonium kinetic isotope effects for the addition of the hydrogen atom to a variety of alkenes have been determined experimentally and theoretically.¹²⁹

Addition to Oxygen-containing Multiple Bonds

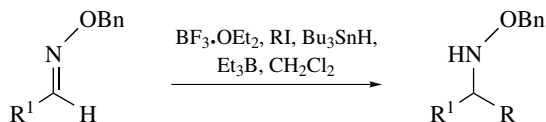
A new free-radical carbonylation strategy, employing *S*-phenyl chlorothioformates and alkyl halides, has been developed.¹³⁰ Reaction with (Bu₃Sn)₂ furnishes the corresponding *S*-phenyl esters in moderate yields (Scheme 30).



SCHEME 30

Addition to Nitrogen-containing Multiple Bonds

Muon spin relaxation (μ SR) has been employed in determining the rate constants and Arrhenius parameters for the addition of the ethyl radical and the *t*-butyl radical to NO.¹³¹ 5-*exo*-Cyclization of aryl radicals on to the nitrogen atom of imidate esters has been reported.³⁵ Intermolecular radical addition to a wide range of aldoxime ethers, using Et₃B as an initiator, to give the corresponding benzyloximines has been studied (Scheme 31). The reaction was accelerated by the addition of BF₃·OEt₂.¹³²



SCHEME 31

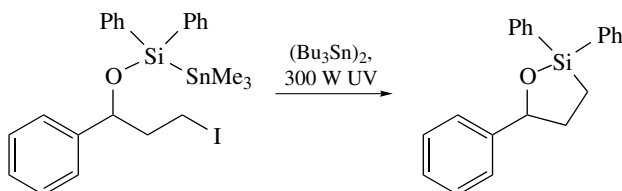
Homolytic Substitution

Aromatic Substitution

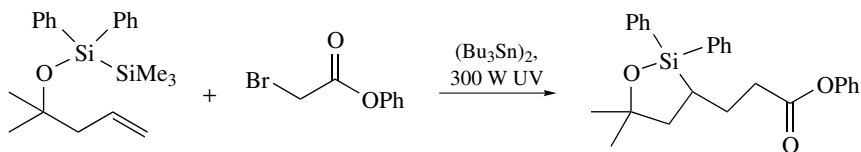
The reactions of bromine and chlorine atoms (generated in aqueous solution) with binuclear and trinuclear aza-arenes have been reported.¹³³ In addition to products arising from substitution of a hydrogen atom by a halogen, oxidation products similar to those found in reactions with hydroxyl radicals were also detected. The detection of aryl radicals in several hydrodediazonization reactions has been observed when iodoacetic acid was used as an aryl-radical trapping agent. All hydrodediazonizations studied were found to proceed through radical intermediates irrespective of whether they were initiated or not.¹³⁴

S_H2 and Related Reactions

Homolytic substitution reactions including homolytic allylation, radical [2,3]-migrations and stereochemical reactions been reviewed. The review also highlights the possible applications of homolytic substitution reactions.²⁰ S_Hi reactions at silicon (by carbon-centred radicals in the α -position of stannylated silyl ethers) are efficient UMCT reactions producing cyclized alkoxy silanes. Bimolecular reactions can also be facilitated in good yield (Schemes 32 and 33).¹³⁵



SCHEME 32



SCHEME 33

Reactivity Effects

Polarity and Philicity

Substituent effects for the regioselectivity of cyclization of vinyl radicals on to aromatic rings have been investigated and the nature of the polar effects suggests that vinyl radicals have slight electrophilic character.¹³⁶ The cyclizations of a range of fluorinated radicals have been studied. When the fluorine was substituted near to the radical centre, great effects on both the rate and the regioselectivity of the process were observed.³⁹ These effects were ascribed to both polar and pyrimidalization effects. An assessment of the nucleophilicity and electrophilicity of radicals, and the polar effects on radical addition reactions, have been determined using principal component analysis (PCA).¹³⁷ The results indicated that the hydroxymethyl radical was strongly nucleophilic, the methyl radical moderately nucleophilic, the *t*-butoxycarbonyl and cyanomethyl radicals mildly nucleophilic, and the phenylsulfonyl and tosyl radicals moderately electrophilic.

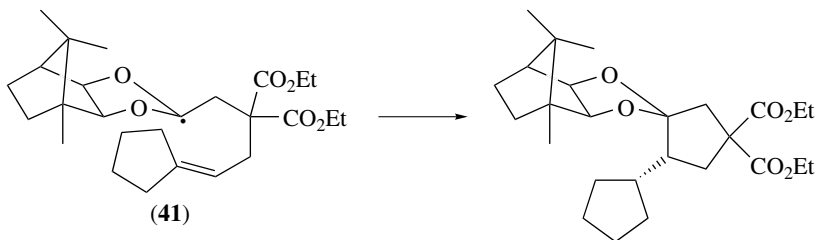
Stability of Radicals

The kinetics of hydrogen abstraction by the CF₃COC(C₂F₅)₂ radical have been studied by ESR with the degree of delocalization calculated using the MNDO/PM3 method.⁷² All aspects of the solution structure, stability, and chemistry of carbon-centred fluorine-containing free radicals have been discussed.¹³⁸

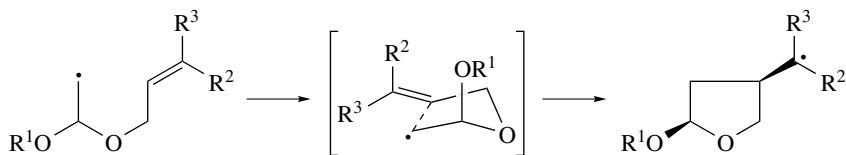
Stereoselectivity in Radical Reactions

Stereoselectivity in Cyclization

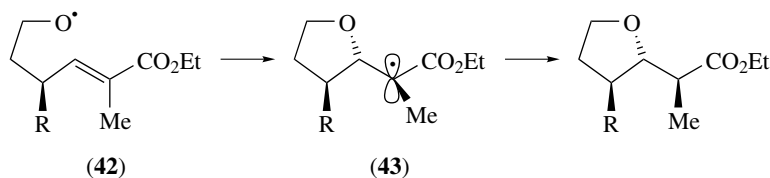
Almost complete stereoselectivity was obtained in the cyclization of the constrained 1,3-dioxabicyclo[4.3.0]nonan-2-yl radical (**41**) (Scheme 34).¹³⁹ Locking the 1,3-dioxolanyl unit into an envelope conformation was found to be important in controlling such 5-*exo* cyclizations. Radical-chain cyclization of alkenyloxysilanes using thiols has been studied.⁴⁹ The stereochemistry of these reactions was determined by steric effects, even in the presence of chiral thiol catalysts. Cyclization of a range of acetals proceeds to give *cis* isomers preferentially, indicating that cyclization takes place via a chair-like transition state with the substituent alkoxy group in the pseudo-axial position (Scheme 35).¹⁴⁰ This unusual stereochemical outcome was postulated to arise due to the anomeric effect. The 5-*exo* oxygen-radical cyclization of (**42**) to (**43**) has been reported. This gives rise to 2,3-*trans*-disubstituted THFs caused by high levels of



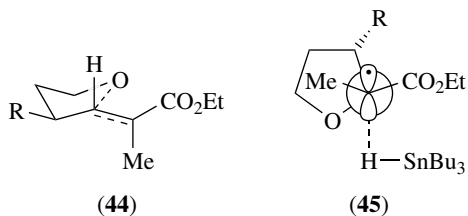
SCHEME 34



SCHEME 35



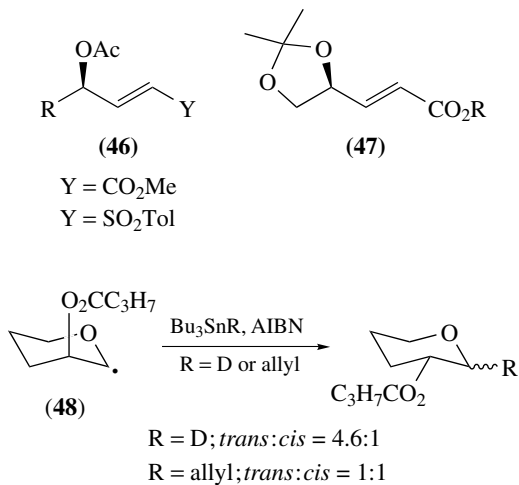
SCHEME 36



1,2-induction in both steps (Scheme 36).¹⁴¹ The steric nature of R was investigated for its effect upon the stereochemical outcome of the reaction. Transition states for both cyclization (44) and reduction (45) were postulated to explain the stereoselectivity.

Stereoselectivity in Addition Reactions

High *anti*-asymmetric induction in the additions of the 1-hydroxy-1-methylethyl radical to (*E*)- γ -hydroxy- α , β -unsaturated esters and sulfones (46) has been observed.¹⁴² Selectivity was greatest with bulkier R groups. In contrast, the *Z*-isomer led to the *syn*-isomers exclusively. This is in contrast to recent work on the addition to



SCHEME 37

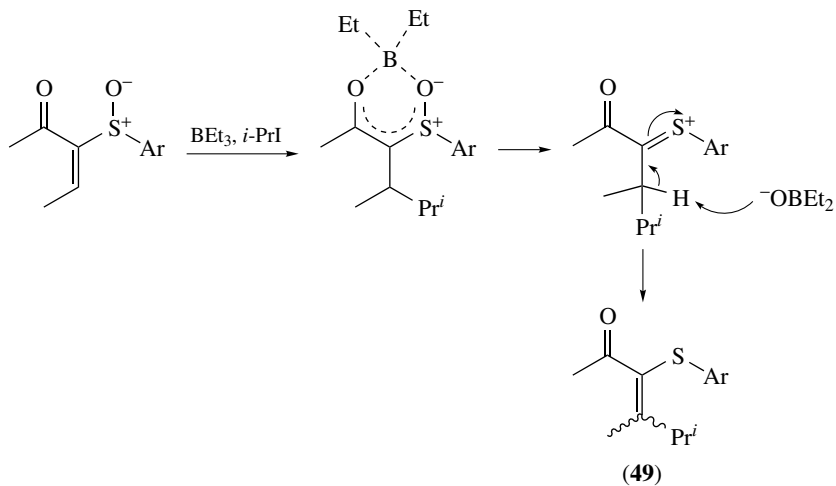
(*E*)-(47) which gives *syn*-isomers as the major products. Observations based on X-ray and NMR analysis and MNDO/PM3 calculations indicated that selectivity arises from attack at the least-hindered side (opposite to the R group in the *E*-compounds) from the conformation with the acetoxy group 'inside' the double bond. For the (*Z*)-alkenes, the same was true but from a conformation with the acetoxy group located 'outside' the alkene.

The influence of the classical anomeric effect and quasi-anomeric effect on the reactivity of various radicals has been probed.¹⁴³ The isomer distribution for the deuteration of radical (48) was found to be selective whereas allylation was non-selective (Scheme 37). The results were explained by invoking a later transition state in the allylation, thus increasing the significance of thermodynamic control in the later reactions. Radical addition to a range of α -(arylsulfonyl)enones has been reported to give unexpected Pummerer rearrangement products (49) (Scheme 38).¹⁴⁴ A mechanism has been postulated proceeding via the boron enolate followed by elimination of Et₂BO⁻ anion.

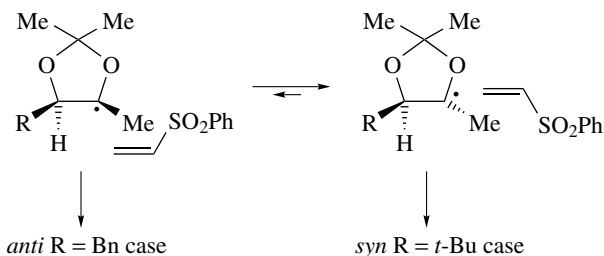
The stereochemical outcome for addition of *t*-1,3-dioxolan-4-yl and oxiranyl radicals to phenyl vinyl sulfone has been probed. The results indicated that the *syn*:*anti* selectivity could be altered by changing the group next to the radical in the dioxolanyl case but not in the oxiranyl case (bulky groups had a large *syn*-directing effect) (Scheme 39).¹⁴⁵ Several alkenyl-lactones and -lactams have been subjected to hydrosilylation conditions using carbohydrate-derived thiols as homochiral polarity reversal catalysts (yields 25–96%; *ee* 5–95%).¹⁴⁶

Stereoselectivity in Atom Transfer

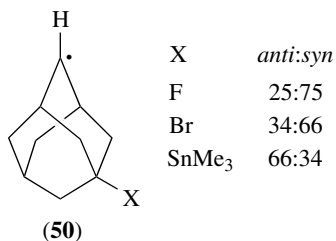
A review on asymmetric induction in hydrogen-transfer and allylation reactions of a range of chiral ester derivatives has highlighted both structural and electronic roles



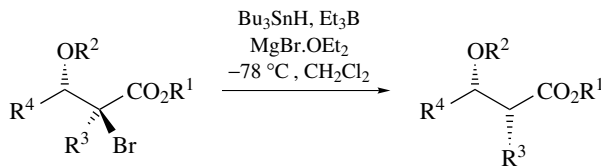
SCHEME 38



SCHEME 39



in controlling selectivity.¹⁹ Diastereoselectivity in D-atom and halogen-atom abstraction reactions mediated by 5-substituted 2-adamantyl radicals (**50**) was shown to be dependent on the electronic character of the 5-substituent.¹⁴⁷ These observations are in accord with both the Cieplak transition-state hyperconjugation model and also the possibility of an early reactant-like TS. The reductions of a range of α -bromo- β -alkoxy esters under chelation-controlled conditions (using MgBr₂·OEt₂ and Bu₃SnH) have been shown to give rise to *syn* products.¹⁴⁸ The effects of substituents at positions

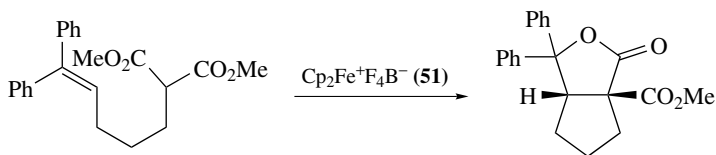


SCHEME 40

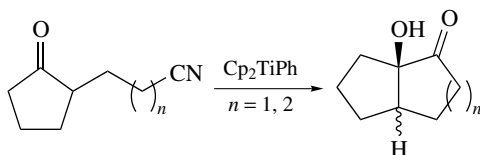
2 and 3, and the role of the ester substituents, were probed and it was found that they had little effect on the stereochemical outcome (Scheme 40). Work by the same authors has shown that the diastereoselectivity of hydrogen-atom transfer in the reactions of acyclic free radicals can be enhanced using a strategy employing bifunctional protecting groups (taking advantage of the ‘exocyclic effect’).¹⁴⁹

Redox Reactions

Various transition metals have been used in redox processes. For example, tandem sequences of cyclization have been initiated from malonate enolates by electron-transfer-induced oxidation with ferricenium ion Cp_2Fe^+ (**51**) followed by cyclization and either radical or cationic termination (Scheme 41).¹⁵⁰ Titanium, in the form of Cp_2TiPh , has been used to initiate reductive radical cyclizations to give γ - and δ -cyano esters in a 5- or 6-*exo* manner, respectively (Scheme 42). The Ti(III) reagent coordinates both to the $\text{C}=\text{O}$ and CN groups and cyclization proceeds irreversibly without formation of iminyl radical intermediates.¹⁵¹ The oxidation of benzylic and allylic alcohols in a two-phase system in the presence of *t*-butyl hydroperoxide, a copper catalyst, and a phase-transfer catalyst has been examined.¹⁵² The reactions were shown to proceed via a heterolytic mechanism; however, the oxidations of related active methylene compounds (without the alcohol functionality) were determined to be free-radical processes.



SCHEME 41



SCHEME 42

Radical Ions

Anion Radicals

Analysis and calculation of features that govern nucleophilic reactivity in $S_{RN}1$ processes have been studied, focusing upon the addition of anions to Ph^{\bullet} . In this addition step, electron transfer to give the radical anion is concerted with bond formation. The extra electron is located in the π^* orbital of the aromatic group.¹⁵³

Cation Radicals

A review on the nitration of aromatics (using a range of species including $\bullet\text{NO}_2$ and $\bullet\text{NO}_3$) has appeared.¹² Evidence for electron-transfer mechanisms via radical cations has been reviewed. In addition, another review comparing the reactivity of a range of radicals and radical cations has appeared.¹⁵ While radicals prefer to add to the carbon of CN triple bonds, radical cations were found to prefer addition at the N atom. *Ab initio* calculations were performed to rationalize this behaviour.

The generation of radical cations by photo-induced SET processes has been reviewed.¹⁵⁴ The reaction between a variety of aromatic compounds and some common halogenating reagents (ICl, Cl_2 , Br_2 , I_2 , NBS, and NCS) in 1,1,1,3,3,3-hexafluoropropan-2-ol has been investigated using EPR.¹⁵⁵ The results indicated that the reactions followed an ET mechanism, where the initial step produces a mixture of $\text{ArH}^{+\bullet}$ and the halide ion, which slowly react to give the observed halogenated aromatics. The fluorinated solvent favours the mechanism by both increasing the oxidative power of the halogen source as well as deactivating the nucleophile.

An SET photo-sensitization technique has been employed to generate and study the decay of anilinium radicals derived by one-electron oxidation of α -anilino-carboxylates, β -anilino alcohols and α -anilinosilanes. In particular, the effects of the electrofugal group, reaction medium, and substituents upon the outcome of the reactions (desilylation, decarboxylation, and retro-aldol cleavage) were studied.¹⁵⁶ Irradiation using sunlight of a TiO_2/MeCN suspension containing 4-methoxybenzyl(trimethyl)silane and maleic anhydride generates a benzyl radical, formed initially from a radical cation derived from the silane.¹⁵⁷

Peroxides, Peroxyl, and Hydroxyl Radicals

Peroxides

The abstraction ability from cyclohexane of radicals derived from dialkyl peroxides has been reported.¹⁵⁸ The experiments were performed with and without the trapping agent MSD (α -methylstyrene dimer), the abstracting species being alkoxy radicals derived from the peroxides. However, some dehydro dimer yields indicated that abstraction was also occurring by alkyl radicals.

The radical chemistry of *t*-butyl hydroperoxide in the oxidation of activated hydrocarbons has been reported.¹⁵⁹

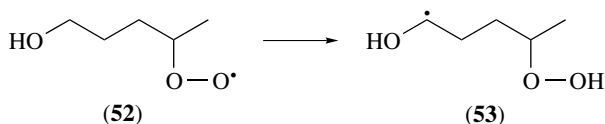
Peroxyl Radicals

A review of peroxy radicals, including rate constants for their formation, solvent effects, and other relevant information, has appeared.¹ In addition, other reviews encompassing the recombination of peroxy radicals,² their reactions in (a) the gas phase,³ (b) aqueous solution,⁴ (c) mixed-solvent systems⁵ and (d) organic solvents⁶ have appeared. Further reviews have dealt with the ESR spectra of peroxy radicals,⁷ the atmospheric chemistry of peroxy radicals,⁸ the chemistry of heteroatom peroxy radicals such as trioxyl, *S*-peroxyl and *N*-peroxyl radicals,⁹ and the reactions of hydroperoxyl radicals with organic and inorganic compounds in aqueous media.¹⁰

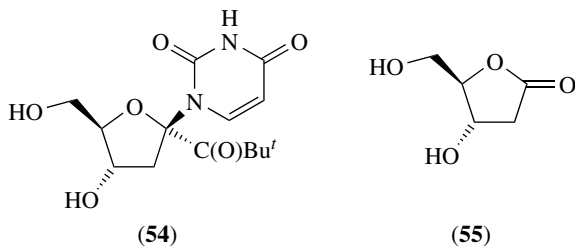
H-abstractions by peroxy radicals have been studied.⁹² Thus, the regioselectivity of hydrogen-atom abstraction from a range of alkyl-substituted aromatics by the α , α -dimethylbenzylperoxyl radical has been examined using MINDO/3 calculations.⁹² The activation energies of intramolecular H-abstraction (1,5-translocation) by the oxygen atom in peroxides have been studied theoretically using density-functional molecular-orbital methods. The results were compared with experimental data and conclusions drawn.¹⁶⁰ An early-transition-state model with charge transfer has been proposed for the reaction of some C–H bonds with peroxy radicals.¹⁶¹ The rate constant for the isomerization of (52) to (53) (an important reaction in atmospheric pollution and low-temperature combustion processes) has been determined [463–523 K; $A(H) = 3.2 \times 10^{10} \text{ s}^{-1}$; $E_a = 16.9 \text{ kcal mol}^{-1}$] (Scheme 43).¹⁶²

The reactivity of a range of alkenes in addition reactions of peroxy radicals has been reported.¹⁶³ Parameters that described the relationship between the activation energy and enthalpy were calculated. An activation energy of 82 kJ mol^{-1} was determined for the addition of alkylperoxy radicals to isolated C=C bonds, rising by 8.5 kJ mol^{-1} when the alkene was conjugated with an aromatic substituent.

The process of oxidative DNA cleavage has been modelled through irradiation of the compound (54). Hence, in the presence of O_2 , H_2O , and photolyzing conditions, (54) gave uracil, lactone (55), and starting material in a 0.15:0.15:1 ratio.¹⁶⁴



SCHEME 43



Hydroxyl Radical

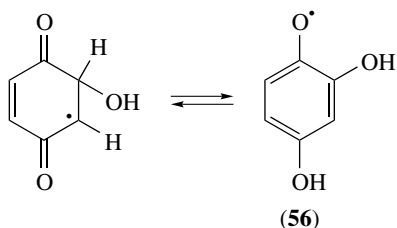
The role of $\bullet\text{OH}$ in ozone chemistry continues to be an important area of research. Thus, one of the first pathways in the production of ozone by hydrocarbons in the troposphere is their reaction with $\bullet\text{OH}$. This reaction has been studied theoretically with a range of simple alkanes, and activation energies were found to increase as one goes from tertiary to secondary to primary hydrocarbons.¹⁶⁵ The competing role of orbital overlap and energy difference on the delocalization energy of the transition state for the reactions of the hydroxyl radical with ethane, propane, and cyclopropane has been examined by both experimental and theoretical analysis.¹⁶⁶ In other studies on the reactivity of $\bullet\text{OH}$ with various functional groups, the absolute rate constants for the reaction of $\bullet\text{OH}$ with acetone, butan-2-one, and three other ketones have been measured using pulsed-laser photolysis-induced fluorescence at 243–372 K.¹⁶⁷ Using relative-rate methods, the rate constants for the reaction between $\bullet\text{OH}$ and a range of methyl esters,¹⁶⁸ dibasic esters,¹⁶⁹ and alcohols¹⁷⁰ (hexan-1-ol, 1-methoxypropan-2-ol, butan-1-ol, 2-butoxyethanol, pentan-1-ol, ethane-1,2-diol, and propane-1,2-diol) have been measured. The tropospheric lifetimes were then estimated and the mechanisms of the reactions discussed in light of the current understanding of atmospheric oxygenated chemistry.¹⁷¹

The oxidative degradations of binuclear azaarenes (quinoline, isoquinoline, and benzodrazines) by hydroxyl and sulfate radicals¹⁷² and halogen radicals¹³³ have been studied under both photochemical and dark-reaction conditions. A shift from oxidation of the benzene moiety to the pyridine moiety was observed in the quinoline and isoquinoline systems upon changing the reaction from the dark to photochemical conditions. The results were interpreted using frontier-orbital calculations. The reaction of $\bullet\text{OH}$ with the dye 3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-(1,8)(2*H*,5*H*)-acridinedione has been studied, and the transient absorption bands assigned in neutral solution.¹⁷³ The redox potential (and also the $\text{p}K_{\text{a}}$ of the transient species) was determined. Hydroxyl radicals have been found to react with thioanisole via both electron transfer to give radical cations (73%) and OH-adduct formation (23%). The bimolecular rate constant was determined ($3.5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$).¹⁷⁴

The reaction of $\bullet\text{OH}$ with HFCs has attracted interest. The temperature dependence of the fast initial $\text{H}\bullet$ abstraction by $\text{HO}\bullet$ in HFCs has been calculated using *ab initio* methods.¹⁷⁵ Rate constants calculated using HF and MP2(G-31G(d)) were found to be substantially greater than those determined experimentally. In other work investigating reactions of $\bullet\text{OH}$ with HFCs, rate constants for its reactions with HFC-245cb (MeCF_2CF_3) and other fluoroalkenes have been determined.¹⁷⁶

Pulsed radiolysis in NO-saturated aqueous solution at a variety of wavelengths has been used to generate hydroxyl radicals and measure the rate of addition to 1,4-benzoquinones. Mechanistically, the kinetic data indicated that the first-formed adduct undergoes a rapid keto–enol tautomerism to give (**56**).¹⁷⁷

In biological chemistry, the reaction of the glycine anion $\text{H}_2\text{NCH}_2\text{CO}_2^-$ with $\text{HO}\bullet$ has been investigated by pulse radiolysis. The major pathway was found to be loss of



SCHEME 44

CO_2 via initial $\cdot\text{OH}$ -induced oxidation to both $\text{H}_2\text{N}^+\text{CH}_2\text{CO}_2^-$ and $\text{HNCH}_2\text{CO}_2^-$ in 63 and 37% yields, respectively. The fragmentation of the radical cation to CO_2 and $\cdot\text{CH}_2\text{NH}_2$ was found to be fairly fast (<100 ns).¹⁷⁸

References

- ¹ Alfassi, Z. V., *Peroxyl Radicals*, 1997, 1; *Chem. Abs.*, **128**, 167006 (1998).
- ² Lesclaux, R., *Peroxyl Radicals*, 1997, 81; *Chem. Abs.*, **128**, 167011 (1998).
- ³ Wallington, T. J., Nielsen, O. J., and Sehested, J., *Peroxyl Radicals*, 1997, 113; *Chem. Abs.*, **128**, 167012 (1998).
- ⁴ Von Sonntag, C. and Schuchmann, H.-P., *Peroxyl Radicals*, 1997, 173; *Chem. Abs.*, **128**, 167013 (1998).
- ⁵ Alfassi, Z. B., Huie, R. E. and Neta, P., *Peroxyl Radicals*, 1997, 235; *Chem. Abs.*, **128**, 167014 (1998).
- ⁶ Howard, J. A., *Peroxyl Radicals*, 1997, 283; *Chem. Abs.*, **128**, 167015 (1998).
- ⁷ Rhodes, C. J., *Peroxyl Radicals*, 1997, 335; *Chem. Abs.*, **128**, 167016 (1998).
- ⁸ Wallington, T. J. and Nielsen, O. J., *Peroxyl Radicals*, 1997, 457; *Chem. Abs.*, **128**, 167019 (1998).
- ⁹ Von Sonntag, C. and Schuchmann, H.-P., *Peroxyl Radicals*, 1997, 439; *Chem. Abs.*, **128**, 167018 (1998).
- ¹⁰ Cabelli, D. E., *Peroxyl Radicals*, 1997, 407; *Chem. Abs.*, **128**, 167017 (1998).
- ¹¹ Hansch, C. and Gao, H., *Chem. Rev.*, **97**, 2995 (1997).
- ¹² Ridd, J. H., *Acta Chem. Scand.*, **52**, 11 (1998).
- ¹³ Hartshorn, M. P., *Acta Chem. Scand.*, **52**, 2 (1998).
- ¹⁴ Beckwith, A. L. J., Crich, D., Duggan, P. J., and Yao, Q., *Chem. Rev.*, **97**, 3273 (1997).
- ¹⁵ De Lijser, H. J. P. and Arnold, D. R., *J. Phys. Chem. A*, **102**, 5592 (1998).
- ¹⁶ Fallis, A. G. and Brinza, I. M., *Tetrahedron*, **53**, 17543 (1997).
- ¹⁷ Mella, M., Fagnoni, M., Freccero, M., Fasani, E., and Albinì, A., *Chem. Soc. Rev.*, **27**, 81 (1998).
- ¹⁸ Dollbier, W. R., *Top. Curr. Chem*, 192, 97 (1997); *Chem. Abs.*, **128**, 12977 (1998).
- ¹⁹ Guindon, Y., Jung, G., Brigitte, O., and William, W., *Synlett*, 1998, 213; *Chem. Abs.*, **128**, 192206 (1998).
- ²⁰ Walton, J. C., *Acc. Chem. Res.*, **31**, 99 (1998).
- ²¹ Lacôte, E. and Renaud, P., *Angew. Chem., Int. Ed. Engl.*, **37**, 2259 (1998).
- ²² Studer, A. and Bossart, M., *J. Chem. Soc., Chem. Commun.*, 1998, 2127.
- ²³ Mueller, A. M. and Chen, P., *J. Org. Chem.*, **63**, 4581 (1998).
- ²⁴ Wang, H.-X., Shang, Z.-N., Chen, L., Pan, Y.-M., and Zhao, X.-Z., *Huaxue Xuebao*, 56, 766 (2000); *Chem. Abs.*, **129**, 244769 (1998).
- ²⁵ Martinez, F. N., Schlegel, H. B., and Newcomb, M., *J. Org. Chem.*, **63**, 3618 (1998).
- ²⁶ Choi, S.-Y., Toy, P. H., and Newcomb, M., *J. Org. Chem.*, **63**, 8609 (1998).
- ²⁷ Horner, J. H., Tanaka, N., and Newcomb, M., *J. Am. Chem. Soc.*, **120**, 10379 (1998).
- ²⁸ Smith, D. A., Nicolaidis, A., Golding, B. T., and Radom, L., *J. Am. Chem. Soc.*, **120**, 10223 (1998).
- ²⁹ Crich, D. and Mo, X.-S., *J. Am. Chem. Soc.*, **120**, 8298 (1998).
- ³⁰ Kim, S. and Cheong, J. H., *J. Chem. Soc., Chem. Commun.*, 1998, 1143.

- ³¹ Tsentalovich, Y. P., Kulic, L. V., Gritsan, N. P., and Yurkovskaya, S. V., *J. Phys. Chem. A*, **102**, 7975 (1998).
- ³² Merényi, G., Lind, J., and Ebersson, L., *Acta Chem. Scand.*, **52**, 62 (1998).
- ³³ Chatgililoglu, C., Timokhin, V. I., and Ballestri, M., *J. Org. Chem.*, **63**, 1327 (1998).
- ³⁴ Ryu, I., Fukushima, H., Okuda, T., Matsui, K., Kambe, N., Sonoda, N., and Komatsu, M., *Synlett*, 1997, 1265; *Chem. Abs.*, **128**, 61187 (1998).
- ³⁵ McClure, C.K., Kiessling, A. J., and Link, J. S., *Tetrahedron*, **54**, 7121 (1998).
- ³⁶ Horner, J. H., Musa, O. M., Bouvier, A., and Newcomb, M., *J. Am. Chem. Soc.*, **120**, 7738 (1998).
- ³⁷ Clark, A. J. and Peacock, J. L., *Tetrahedron Lett.*, **39**, 1265 (1998).
- ³⁸ Clark, A. J. and Peacock, J. L., *Tetrahedron Lett.*, **39**, 6029 (1998).
- ³⁹ Dolbier, W. R., Rong, X. X., Bartberger, M. D., Koroniak, H., Smart, B. E., and Yang, Z.-Y., *J. Chem. Soc., Perkin Trans. 2*, 1998, 219.
- ⁴⁰ Dolbier, W. R., Li, A., Smart, B. E., and Yang, Z.-Y., *J. Org. Chem.*, **63**, 5867 (1998).
- ⁴¹ Ikeda, M., Ohtani, S., Yamamoto, T., Sato, T., and Ishibashi, H., *J. Chem. Soc., Perkin Trans 1*, 1998, 1763.
- ⁴² Ishibashi, H., Higuchi, M., Ohba, M., and Ikeda, M., *Tetrahedron Lett.*, **39**, 75 (1998).
- ⁴³ Boiteau, L., Boivin, J., Quiclet-Sire, B., Saunier, J.-B., and Zard, S. Z., *Tetrahedron*, **54**, 2087 (1998).
- ⁴⁴ Philippou, A., Degueil-Castaing, M., Beckwith, A. L. J., and Maillard, B., *J. Org. Chem.*, **63**, 6814 (1998).
- ⁴⁵ Simakov, P. A., Martinez, F. N., Horner, J. H., and Newcomb, M., *J. Org. Chem.*, **63**, 1226 (1998).
- ⁴⁶ Musa, O. M., Choic, S.-Y., Horner, J. H., and Newcomb, M., *J. Org. Chem.*, **63**, 786 (1998).
- ⁴⁷ Godfrey, C. R. A., Hegarty, P., Motherwell, W. B., and Uddin, M. K., *Tetrahedron Lett.*, **39**, 723 (1998).
- ⁴⁸ Topiwala, U. P., Luszniak, M. C., and Whiting, D. A., *J. Chem. Soc., Perkin Trans. 1*, 1998, 1185.
- ⁴⁹ Cai, Y. and Roberts, B. P., *J. Chem. Soc., Perkin Trans. 1*, 1998, 467.
- ⁵⁰ Gillmore, J. G. and Tanko, J. M., *Tetrahedron Lett.*, **39**, 8795 (1998).
- ⁵¹ Rigby, J. H., Danca, D. M., and Horner, J. H., *Tetrahedron Lett.*, **39**, 8413 (1998).
- ⁵² Montecvecchi, P. C. and Navacchia, M. L., *J. Org. Chem.*, **63**, 537 (1998).
- ⁵³ Handa, S., Pattenden, G., and Li, W.-S., *J. Chem. Soc., Chem. Commun.*, 1998, 311.
- ⁵⁴ Boffey, R. J., Santagastino, M., Whittingham, W. G., and Kilburn, J. D., *J. Chem. Soc., Chem. Commun.*, 1998, 1875.
- ⁵⁵ Lee, E., Yoon, C. H., Lee, T. H., Kim, S. Y., Ha, T. J., Sung, Y.-S., Park, S.-H., and Lee, S., *J. Am. Chem. Soc.*, **120**, 7469 (1998).
- ⁵⁶ Leardini, R., Nanni, D., Tundo, A., and Zanardi, G., *Tetrahedron Lett.*, **39**, 2441 (1998).
- ⁵⁷ Pesa, M., Pilling, M. J., Robertson, S. H., and Wardlaw, D. M., *J. Phys. Chem. A*, **102**, 8526 (1998).
- ⁵⁸ Naroznik, M., *J. Chem. Soc., Faraday Trans.*, **94**, 2531 (1998).
- ⁵⁹ Naroznik, M. and Niedzielski, J., *J. Chem. Soc., Faraday Trans.*, **94**, 2541 (1998).
- ⁶⁰ Fukaya, H., Ono, T., and Abe, T., *J. Comput. Chem.*, **19**, 277 (1998); *Chem. Abs.*, **128**, 192233 (1998).
- ⁶¹ Skains, P. W., Robertson, S. H., Pilling, M. J., Wardlaw, D. M., Nesbitt, F. L., Peyton Thorn, R., Payne, W. A., and Stief, L. J., *J. Phys. Chem. A*, **101**, 9974 (1997).
- ⁶² Lee, W. T. and Masel, R. L., *J. Phys. Chem. A*, **102**, 2332 (1998).
- ⁶³ Zhang, X.-M., *J. Org. Chem.*, **63**, 1872 (1998).
- ⁶⁴ Trindle, C. and Romberg, K., *J. Phys. Chem. A*, **102**, 270 (1998).
- ⁶⁵ Geimer, J., Beckert, D., and Jenichen, A., *Chem. Phys. Lett.*, **280**, 353 (1997); *Chem. Abs.*, **128**, 127650 (1998).
- ⁶⁶ Lossack, A. M., Rodunov, E., and Bartels, D. M., *J. Phys. Chem. A*, **102**, 7462 (1998).
- ⁶⁷ Kamo, T. and Yamada, M., *Int. J. Chem. Kinet.*, **30**, 923 (1998).
- ⁶⁸ Hranisavljevic, J., Carroll, J. J., Su, M.-C., and Michael, J. V., *Int. J. Chem. Kinet.*, **30**, 859 (1998).
- ⁶⁹ Bapat, J. B., Brown, R. F. C., Bulmer, G. H., Childs, T., Coulston, K. J., Eastwood, F. W., and Taylor, D. K., *Aust. J. Chem.*, **50**, 1159 (1998).
- ⁷⁰ Petrov, L. V. and Solyanikov, V. M., *Nefekhimiya*, **38**, 128 (1998); *Chem. Abs.*, **129**, 161252 (1998).
- ⁷¹ Dolbier, W. R. and Li, A.-R., *J. Chem. Soc., Perkin Trans. 2*, 1998, 79.
- ⁷² Shaposhnikova, E. N., Avetisyan, E. A., Sterlin, S. R., Bubnov, N. N., Solodovnikov, C. P., Chistyakov, A. L., Stankevich, I. V., and Tumanski, B. L., *Russ. Chem. Bull.*, **46**, 1851 (1997); *Chem. Abs.*, **128**, 180118 (1998).
- ⁷³ Milanovanovic, J. N. and Joksovic, M., *J. Serb. Chem. Soc.*, **63**, 143 (1998); *Chem. Abs.*, **128**, 2017012 (1998).
- ⁷⁴ Peeters, D. and Leroy, G., *Eur. J. Org. Chem.*, 1998, 1397.
- ⁷⁵ Dakternieks, D., Henry, D. J., and Schiesser, C. H., *J. Chem. Soc., Perkin Trans. 2*, 1998, 591.

- ⁷⁶ Canning, P. S. J., McCrudden, K., Maskill, H., and Sexton, B., *J. Chem. Soc., Chem. Commun.*, 1998, 1971.
- ⁷⁷ Braslau, R. and Anderson, M. O., *Tetrahedron Lett.*, **39**, 4227 (1998).
- ⁷⁸ Zavitsas, A., *J. Am. Chem. Soc.*, **120**, 6578 (1998).
- ⁷⁹ Rauk, A., Yu, D., and Armstrong, D. A., *J. Am. Chem. Soc.*, **120**, 8848 (1998).
- ⁸⁰ Cai, Y. and Roberts, B. P., *J. Chem. Soc., Chem. Commun.*, 1998, 1145.
- ⁸¹ Schiesser, C. H. and Skidmore, M. A., *J. Chem. Soc., Perkin Trans. 2*, 1998, 2329.
- ⁸² Blank, D. A., Hemmi, N., Suits, A. G., and Lee, Y. T., *Chem. Phys.*, **231**, 261 (1998); *Chem. Abs.*, **129**, 108764 (1998).
- ⁸³ Mellouki, A., *J. Chim. Phys. Phys.-Chim. Biol.*, **95**, 513 (1998); *Chem. Abs.*, **128**, 270370 (1998).
- ⁸⁴ Ayhens, Y. V., Nicovich, J. M., McKee, M. L., and Wine, P. H., *J. Phys. Chem. A*, **101**, 9382 (1997).
- ⁸⁵ Jodkowski, J. T., Rayez, M.-T., Rayez, J.-C., Bérces, T., and Dóbbé, S., *J. Phys. Chem. A*, **102**, 9219 (1998).
- ⁸⁶ Jodkowski, J. T., Rayez, M.-T., Rayez, J.-C., Bérces, T., and Dóbbé, S., *J. Phys. Chem. A*, **102**, 9230 (1998).
- ⁸⁷ Kambanis, K. G., Lazarou, Y. G., and Papagiannakopoulos, P., *J. Phys. Chem. A*, **102**, 8620 (1998).
- ⁸⁸ Louis, F. and Sawerysyn, J.-P., *J. Chem. Soc., Faraday Trans.*, **94**, 1437 (1998).
- ⁸⁹ Schested, J., Christensen, L. K., Nielsen, O. L., and Wallington, T. J., *Int. J. Chem. Kinet.*, **30**, 913 (1998).
- ⁹⁰ Li, Z.-H., Wu, L.-M., and Liu, R.-Z., *Huaxue Xuebao*, **55**, 1061 (1997); *Chem. Abs.*, **128**, 34435 (1998).
- ⁹¹ Stutz, J., Ezell, M. J., Ozell, A. A., and Finlayson-Pitts, B. J., *J. Phys. Chem. A*, **102**, 8510 (1998).
- ⁹² Dmitruk, A., *Russ. J. Org. Chem.*, **33**, 1801 (1997); *Chem. Abs.*, **129**, 202592 (1998).
- ⁹³ Jursic, B. S., *THEOCHEM*, **428**, 49 (1998); *Chem. Abs.*, **128**, 308124 (1998).
- ⁹⁴ Zavitsas, A. A., *J. Chem. Soc., Perkin Trans. 2*, 1998, 499.
- ⁹⁵ Hawkins, C. L. and Davies, M. J., *J. Chem. Soc., Perkin Trans. 2*, 1998, 1937.
- ⁹⁶ Galli, C. and Pav, T., *Tetrahedron*, **54**, 2893 (1998).
- ⁹⁷ Crich, D. and Recupero, F., *J. Chem. Soc., Chem. Commun.*, 1998, 189.
- ⁹⁸ Schiesser, C. H. and Wild, L. M., *J. Org. Chem.*, **63**, 670 (1998).
- ⁹⁹ Berry, R. J. and Marshall P., *Int. J. Chem. Kinet.*, **30**, 179 (1998).
- ¹⁰⁰ Bottoni, A., *J. Phys. Chem. A*, **102**, 10142 (1998).
- ¹⁰¹ Meinike, T., Engelmann, L., Olzmann, M., and Scherzer, K., *Int. J. Chem. Kinet.*, **30**, 721 (1998).
- ¹⁰² Long, Z.-Y. and Chen, Q.-Y., *J. Fluorine Chem.*, **91**, 91 (1998); *Chem. Abs.*, **129**, 230335 (1998).
- ¹⁰³ Fletcher, B., Kammrudin Suleman, N., and Tanko, J. M., *J. Am. Chem. Soc.*, **120**, 11839.
- ¹⁰⁴ Dneprovskii, A. S., Kuznetsov, D. V., Eliseenkov, E. V., Fletcher, B., and Tanko, J. M., *J. Org. Chem.*, **63**, 8860 (1998).
- ¹⁰⁵ Resende, S. M., Pliego, J. R., and De Almeida, W. B., *J. Chem. Soc., Faraday Trans.*, **94**, 2895 (1998).
- ¹⁰⁶ Stutz, J., Ezell, M. J., and Finlayson-Pitts, B. J., *J. Phys. Chem. A*, **101**, 9187 (1997).
- ¹⁰⁷ Stutz, J., Ezell, M. J., and Finlayson-Pitts, B. J., *J. Phys. Chem. A*, **102**, 6056 (1998).
- ¹⁰⁸ Seetula, J. A., *J. Chem. Soc., Faraday Trans.*, **94**, 3561 (1998).
- ¹⁰⁹ Paleta, O., Cirkva, V., Budkova, Z., and Bohm, S., *J. Fluorine Chem.*, **86**, 155 (1997); *Chem. Abs.*, **128**, 114604 (1998).
- ¹¹⁰ Arnaud, R., Vetere, V., and Barone, V., *Chem. Phys. Lett.*, **293**, 295 (1998); *Chem. Abs.*, **129**, 260008 (1998).
- ¹¹¹ Arnaud, R., Bugand, N., Vetere, V., and Barone, V., *J. Am. Chem. Soc.*, **120**, 5733 (1998).
- ¹¹² Wong, M. W. and Radom, L., *J. Phys. Chem. A*, **102**, 2237 (1998).
- ¹¹³ Radom, L. and Wong, M. W., *ACS Symp. Ser.*, **685**, 31 (1998); *Chem. Abs.*, **128**, 204514 (1998).
- ¹¹⁴ Delest, B., Shtareu, A. B., and Dolbier, W. R., *Tetrahedron*, **54**, 9273 (1998).
- ¹¹⁵ Korchowiec, J. and Uchimaru, T., *J. Phys. Chem. A*, **102**, 6682 (1998).
- ¹¹⁶ Hudson, A., Waterman, D., Della Bona, M. A., Alberti, A., Altieri, A., Benaglia, M., and Mac-ciantelli, D., *J. Chem. Soc., Perkin Trans. 2*, 1998, 2255.
- ¹¹⁷ Weber, M. and Fischer, H., *Helv. Chim. Acta*, **81**, 770 (1998).
- ¹¹⁸ Park, J. S. B. and Walton, J. C., *J. Chem. Soc., Perkin Trans. 2*, 1997, 2579.
- ¹¹⁹ Pérez-Casany, M. P., Nebot-Gil, I., Sánchez-Marín, J., Tomás-Vert, F., Martínez-Ataz, E., Cabanas-Galán, B., and Aranda-Rubio, A., *J. Org. Chem.*, **63**, 6978 (1998).
- ¹²⁰ Bedjanian, Y., Poulet, G., and Le Bras, G., *J. Phys. Chem. A*, **102**, 5867 (1998).
- ¹²¹ Gilbert, B. C., Lindsay Smith, J. R., Ward, S. R., Whitwood, A. C., and Taylor, P., *J. Chem. Soc., Perkin Trans. 2*, 1998, 1565.
- ¹²² Hwu, J. R., King, K. Y., Wu, I.-F., and Hakimelahi, G. H., *Tetrahedron Lett.*, **39**, 3721 (1998).
- ¹²³ Dang, H.-S., Kim, K.-M., and Roberts, B. P., *J. Chem. Soc., Perkin Trans. 1*, 1998, 1613.

- 124 Dang, H.-S. and Roberts, B. P., *J. Chem. Soc., Perkin Trans. 1*, 1998, 67.
- 125 Xiang, J., Everts, J., Rivkin, A., Curran, D. P., and Fuchs, P. L., *Tetrahedron Lett.*, **39**, 4163 (1998).
- 126 Percec, V., Barboiu, B., and Kim, H.-J., *J. Am. Chem. Soc.*, **120**, 305 (1998).
- 127 Bernardoni, S., Lucarini, M., Pedulti, G. F., Valgimigli, L., Gevorgyan, V., and Chatgililoglu, C., *J. Org. Chem.*, **62**, 8009 (1997).
- 128 Eberson, L. and Persson, O., *Acta Chem. Scand.*, **52**, 1081 (1998).
- 129 Villá, J., Corchado, J. C., González-Lafont, A., Lluch, J. M., and Truhlar, A. G., *J. Am. Chem. Soc.*, **120**, 12141 (1998).
- 130 Kim, S. and Jan, S. Y., *J. Chem. Soc., Chem. Commun.*, 1998, 815.
- 131 Dilger, H., Stolmar, M., Himmer, U., and Roduner, E., *J. Phys. Chem. A*, **102**, 6772 (1998).
- 132 Miyabe, H., Shibata, R., Ushiro, C., and Naito, T., *Tetrahedron Lett.*, **39**, 631 (1998).
- 133 Beitz, T., Bechmann, W., and Mitzner, R., *J. Phys. Chem. A*, **102**, 6766 (1998).
- 134 Wassmundt, F. W. and Kiesman, W. F., *J. Org. Chem.*, **62**, 8304 (1997).
- 135 Studer, A., *Angew. Chem., Int. Ed. Engl.*, **37**, 462 (1998).
- 136 Montevocchi, P. C. and Navacchia, M. L., *J. Org. Chem.*, **63**, 537 (1998).
- 137 Héberger, K. and Lopata, A., *J. Org. Chem.*, **63**, 8646 (1998).
- 138 Dolbier, W. R., *Top. Curr. Chem.*, **192**, 97 (1997); *Chem. Abs.*, **128**, 12977 (1998).
- 139 Stien, D., Crich, D., and Bertrand, M. P., *Tetrahedron*, **54**, 10779 (1998).
- 140 Beckwith, A. L. J. and Page, D. M., *J. Org. Chem.*, **63**, 5144 (1998).
- 141 Guindon, Y. and Denis, R. C., *Tetrahedron Lett.*, **39**, 339 (1998).
- 142 Ogura, K., Kayano, A., and Akazome, M., *Bull. Chem. Soc. Jpn.*, **70**, 3091 (1997).
- 143 Beckwith, A. L. J. and Duggan, P. J., *Tetrahedron*, **54**, 6929 (1998).
- 144 Mase, N., Watanabe, Y., Ueno, Y., and Toru, T., *J. Chem. Soc., Chem. Commun.*, 1998, 1413.
- 145 Gerster, M. and Renaud, P., *Synthesis*, **11**, 1261 (1997); *Chem. Abs.*, **128**, 88450 (1998).
- 146 Hague, M. B., Roberts, B. P., and Tocher, D. A., *J. Chem. Soc., Perkin Trans. 1*, 1998, 2881.
- 147 Adcock, W., Lünsmann, D., and Trout, N. A., *J. Org. Chem.*, **63**, 7231 (1998).
- 148 Guindon, Y. and Rancourt, J., *J. Org. Chem.*, **63**, 6554 (1998).
- 149 Guindon, Y., Faucher, A.-M., Bourque, E., Caron, V., Jung, G., and Landry, S. R., *J. Org. Chem.*, **62**, 9276 (1997).
- 150 Jahn, U. and Hartmann, P., *J. Chem. Soc., Chem. Commun.*, 1998, 209.
- 151 Yamamoto, Y., Matsumi, D., and Itoh, K., *J. Chem. Soc., Chem. Commun.*, 1998, 875.
- 152 Rothenberg, G., Feldberg, L., Wiener, H., and Sasson, Y., *J. Chem. Soc., Perkin Trans. 2*, 1998, 2429.
- 153 Galli, C. and Gentili, P., *Acta Chem. Scand.*, **52**, 67 (1998).
- 154 Mella, M., Fagnoni, M., Freccero, M., Fasani, E., and Albini, A., *Chem. Soc. Rev.*, **27**, 81 (1998).
- 155 Eberson, L., Hartshorn, M. P., Radner, F., and Persson, O., *J. Chem. Soc., Perkin Trans. 2*, 1998, 59.
- 156 Su, Z., Mariano, P. S., Falvey, D. E., Yoon, U. C., and Oh, S. W., *J. Am. Chem. Soc.*, **120**, 10676 (1998).
- 157 Cermenati, L., Richter, C., and Albini, A., *J. Chem. Soc., Chem. Commun.*, 1998, 805.
- 158 Watanabe, Y., Ishigaki, H., Okada, H., and Suyama, S., *Poym. J.*, **29**, 940 (1997); *Chem. Abs.*, **128**, 88451 (1998).
- 159 Barton, D. H. R. and Le Gloahec, V. N., *Tetrahedron*, **54**, 15457 (1998).
- 160 Chan, W.-T., Hamilton, I. P., and Pritchard, H. D., *J. Chem. Soc., Faraday Trans.*, **94**, 2303 (1998).
- 161 Opeida, I. A., Dmitruk, A. F., and Zarechnaya, O. M., *Theor. Exp. Chem.*, **33**, 5 (1997); *Chem. Abs.*, **127**, 318594 (1997).
- 162 Perrin, O., Heisee, A., Sahetchian, K., Kerhoas, L., and Einhorn, J., *Int. J. Chem. Kinet.*, **30**, 875 (1998).
- 163 Denisova, T. G. and Denisova, E. T., *Neftekhimiya*, **38**, 15 (1998); *Chem. Abs.*, **129**, 54052 (1998).
- 164 Chatgililoglu, C. and Crimisis, T., *J. Chem. Soc., Chem. Commun.*, 1998, 1249.
- 165 Garcia, I., Uc, V., Vivier-Bunge, A., and Smeyers, Y. G., *Comput. Chem. Chem. Eng., Proc. UNAM-CRAY Supercomput. Conf., 3rd*, **1996**, 168 (1997); *Chem. Abs.*, **128**, 167038 (1998).
- 166 Clarke, J. S., Kroll, J. R., Donahue, N. M., and Anderson, J. G., *J. Phys. Chem. A*, **102**, 9847 (1998).
- 167 Le Calvé, S., Hitier, D., Le Bras, G., and Mellovki, A., *J. Phys. Chem. A*, **102**, 4579 (1998).
- 168 Le Calvé, S., Le Bras, G., and Mellovki, A., *J. Phys. Chem. A*, **101**, 9137 (1997).
- 169 Aschmann, S. M. and Atkinson, R., *Int. J. Chem. Kinet.*, **30**, 471 (1998).
- 170 Aschmann, S. M. and Atkinson, R., *Int. J. Chem. Kinet.*, **30**, 533 (1998).
- 171 Baxley, J. S. and Wells, J. R., *Int. J. Chem. Kinet.*, **30**, 745 (1998).
- 172 Beitz, T., Bechmann, W., and Mitzner, R., *J. Phys. Chem. A*, **102**, 6760 (1998).
- 173 Mohan, H., Mittal, J. P., Venkatachalapathy, B., Srividya, N., and Ramamurthy, P., *J. Chem. Soc., Faraday Trans.*, **94**, 4269 (1997).
- 174 Mohan, H. and Mittal, J. P., *J. Phys. Chem. A*, **101**, 10012 (1997).

- ¹⁷⁵ Schwartz, M., Marshall, P., Berry, R. J., Ehlers, C. J., and Petersson, G. A., *J. Phys. Chem. A*, **102**, 10074 (1998).
- ¹⁷⁶ Orkin, V. L., Huie, R. E., and Kurylo, M. J., *J. Phys. Chem. A*, **101**, 9118 (1997).
- ¹⁷⁷ Schuhmann, M. N., Bothe, E., von Sonntag, J., and von Sonntag, C., *J. Chem. Soc., Perkin Trans. 2*, 1998, 791.
- ¹⁷⁸ Bonifacic, M., Stefanic, I., Hug, G. L., Armstrong, D. A., and Asmus, K.-D., *J. Am. Chem. Soc.*, **120**, 9930 (1998).