Organic Reaction Mechanisms - 1998: An Annual Survey Covering the Literature Dated December 1997 to November 1998. Edited by A. C. Knipe and W. E. Watts

ISBN: 0-471-49017-2

CHAPTER 5

Oxidation and Reduction

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Oxidation by Metal Ions and Related Species

Chromium, Manganese, and Nickel

Chromium(III) catalyses the cerium(IV) oxidation of primary and secondary alcohols in a mixture of H_2SO_4 and $HClO_4$.[1] Kinetic results have been interpreted in terms of the formation of chromium(IV) in a reversible equilibrium, which forms a complex with the alcohol. Internal oxidation–reduction occurs in a rate-determining step to give aldehyde or ketone and regenerate the catalyst in the +3 state. The oxidation of ethanol under similar conditions has also been studied.[2]

The oxidation of alkyl aryl sulfides to sulfoxides with oxochromium(V) complexes is first order in oxidant and in substrate.[3] The better correlation of log k with σ^+ rather than σ and the low magnitude of ρ^+ value (-1.19) were interpreted as evidence for a rate-determining single-electron-transfer mechanism. This was further supported by good correlation in the plots of log k versus oxidation potential/ionization energy.

The kinetics of the oxidation of oxalic acid with chromium(VI) have been studied in acidic and neutral media.[4] In the absence of an acidic medium, a mechanism with an intermediate open-chain ester is proposed. H_2SO_4 and $HClO_4$ were found to decrease the reaction rate and $MeCO_2H$ increased it; this is accounted for by a mechanism in which $HOCrO_2OC(O)Me$ and $MeCO_2CrO_2OC(O)Me$ are intermediates when acetic acid is present. The oxidation of dimethyl sulfoxide by chromium(VI) involves nucleophilic attack of the sulfur of DMSO on chromium, leading to a DMSO–chromate ester, $Me_2S(O^-)-Cr(=O)_2X$ (where $X = ClO_4$ or HSO_4 for reactions in $HClO_4$ or H_2SO_4, respectively), which subsequently decomposes to chromium(IV) and dimethyl sulfone.[5] This reaction is promoted by picolinic acid (PA), which, acting as a bidentate ligand, forms a complex with chromium in a pre-equilibrium step.[6] Nucleophilic attack of the sulfur of DMSO on the Cr(VI)–PA complex leads to the build-up of positive charge on sulfur, accounting for the rate acceleration observed upon addition of the anionic surfactant sodium dodecyl sulfate and the retardation induced by the cationic surfactant cetyl pyridinium chloride. The oxidation of 2-pyridinecarboxaldehyde by dichromate has an unusual mixed fourth-order rate law: first order each in $[H^+]$ and [Cr(VI)] and second order in [aldehyde].[7] In the oxidation of pyridoxal by dichromate, the reduction of Cr(VI) to Cr(III) proceeds through a Cr(V) intermediate complex that was detected by ESR.[8] A polar transition state involving electron transfer from sulfur to Cr(VI) is proposed in the oxidation of dialkyl and alkyl phenyl sulfides.[9] A ternary complex is proposed in the oxidation of substituted *S*-phenylmercaptoacetic acids by chromic acid.[10]

Kinetic studies of the oxidation of some α-hydroxy acids with pyridinium dichromate (PDC) are consistent with a mechanism involving the loss of H_2O from the protonated substrate in the rate-determining step.[11] The oxidation of 8-hydroxyquinoline (oxine) by PDC has been studied.[12] The intermediacy of an acetochromate ion in the oxidation of some acetophenone oximes with PDC is suggested.[13]

The pyridinium chlorochromate (PCC) oxidations of pentaamine cobalt(III)-bound and unbound mandelic and lactic acids have been studied and found to proceed at similar rates.[14] Free-energy relationships in the oxidation of aromatic anils by PCC have been studied.[15] Solvent effects in the oxidation of methionine by PCC[16] and pyridinium bromochromate (PBC)[17] have been investigated; the reaction leads to the formation of the corresponding sulfoxide and mechanisms have been proposed. The major product of the acid-catalysed oxidation of a range of diols by PBC is the hydroxyaldehyde. The reaction is first order with respect to the diol and exhibits a substantial primary kinetic isotope effect.[18] Proposed acid-dependent and acid-independent mechanisms involve the rapid formation of a chromate ester in a pre-equilibrium step, followed by rate-determining hydride ion transfer via a cyclic intermediate. PBC oxidation of thio acids has been studied.[19]

Correlation of structure and reactivity in the oxidation of substituted aromatic anils by pyridinium fluorochromate (PFC) has been attempted using Grunwald–Winstein and Hammett equations.[20] The stoichiometry between the substrate and oxidant is 1:2 in the oxidation of cyclic ketones by PFC to 1,2-diketones.[21] PFC oxidation of secondary alcohols has been investigated.[22]

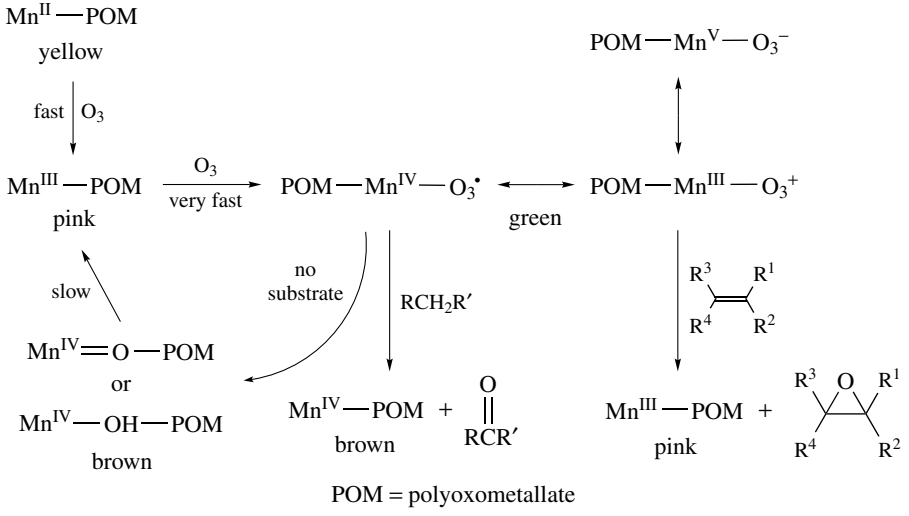
Following earlier studies of the oxidation of formic and oxalic acids by pyridinium fluoro-, chloro-, and bromo-chromates, Banerji and co-workers have studied the kinetics of oxidation of these acids by 2, 2′-bipyridinium chlorochromate (BPCC) to CO_2.[23] The formation constant of the initially formed BPCC–formic acid complex shows little dependence on the solvent, whilst a more variable rate constant for its decomposition to products correlates well with the cation-solvating power. This indicates the formation of an electron-deficient carbon centre in the transition state, possibly due to hydride transfer in an anhydride intermediate HCOO–Cr(=O)(OH)(Cl)–O–bpyH. A cyclic intermediate complex, in which oxalic acid acts as a bidentate ligand, is proposed to account for the unfavourable entropy term observed in the oxidation of this acid.

Quinolinium dichromate (QDC) oxidations of primary[24] and secondary[25] alcohols both proceed via a cyclic chromate ester. Acrylonitrile polymerization was observed in the oxidation of several *para*- and *meta*-substituted benzaldehydes to the corresponding benzoic acids by quinolinium chlorochromate (QCC).[26] QCC oxidations of diphenacyl sulfide[27] and of aromatic anils[28] have been studied.

Steric effects dominate in the oxidation of dialkyl, alkyl phenyl and benzal methyl phenyl sulfides to their sulfoxides by quinolinium fluorochromate (QFC) in aqueous acetic acid.[29] QFC oxidation of phenoxyacetic acids has been studied.[30] Imidazolium dichromate oxidations of α-hydroxy acids have been studied.[31,32]

The kinetics of the manganese(II)- and cerium(III)-catalysed Belusov–Zhabotinsky (BZ) oscillatory reactions were studied with mixed organic acid–ketone substrates.[33] In this mixed substrate system, mandelic acid derivatives are oxidized by the metal, whilst the ketone is brominated and has minimal interaction with the metal. Ketone enolization is shown to be the rate-determining step. Manganese(II) and $[Fe(phen)_3]^{2+}$ are employed as coupled catalysts in a BZ-type reaction with amino acids or peptides as organic substrates.[34] Both components are required for oscillations: manganese(II) catalyses the oxidation of the substrate by BrO_3^- to produce intermediates which reduce bromine to bromide, catalysed by $[Fe(phen)_3]^{2+}$. Manganous sulfate [Mn(II)] and cerium(IV) sulfate were employed as catalysts in a BZ system with 4-methoxy-3-hydroxybenzaldehyde (vanillin) as the substrate.[35] Measurement of the potential for the oxidation of vanillin in the presence of catalyst and acidic potassium bromate shows a two-phase oscillatory system in which the first phase has a greater frequency than the second. The second phase begins when sufficient vanillic acid (the oxidation product) is present. A survey of experimental data on spiral waves in the BZ reaction has been made[36] and compared with several models and numerical simulations. The inhibition of the manganese(II)-catalysed, oscillating Briggs–Raucher reaction by bromide ion is accounted for by the formation of IBr through the reaction of bromide and HOI. IBr competes with I_2 in the iodination of the substrate, malonic acid. Thus the growth of iodide ion, and hence the oscillations, is prevented.[37]

The oxidative stability of polyoxometallates and analogues substituted with transition metals has allowed them to be studied in place of metalloporphyrins in catalysed oxidations, for example with ozone.[38] Alkanes have been oxidized with high selectivity to ketones using $Li_{12}[Mn^{II}{}_2{-}ZnW(ZnW_9O_{34})_2]$ in *t*-butanol–water with ozone as the terminal oxidant. For example, ethylbenzene is oxidized to acetophenone, with only a small amount of 1-phenylethanol formed (85:15; 82% conversion). This selectivity is contrary to manganese porphyrin hydroxylations with ozone, where the alcohol is the major product. The use of lithium cations circumvents the problem of self-oxidation of the quaternary ammonium cations that are normally used to transfer polyoxometallates into organic solvents. The mechanism of the reaction has been investigated using UV–visible and ESR spectroscopy. Coupled with the observations that cumene gives acetophenone and *cis*-decalin forms *trans*-decalol as the major product, the results have been interpreted in terms of the mechanism summarized in Scheme 1. The key intermediate, a green compound, is postulated to be a manganese ozonide complex, and the ESR spectrum is attributed to this species formulated as $POM{-}Mn^{IV}{-}O{-}O{-}O^{\bullet}$. Epoxidation of alkenes also occurs under these conditions with retention of stereochemistry, which is explained in terms of reaction of the ozonide ($POM{-}Mn^{III}{-}O{-}O{-}O^{+}$ canonical form) as an electrophile with the nucleophilic alkene.



SCHEME 1

Kinetic studies on the oxidation of glutamate by manganese(III) in aqueous sulfuric acid, acetic acid, and pyrophosphate suggest different mechanisms for each case.[39] In all cases there is evidence for the involvement of free radicals and in the case of acetic acid and pyrophosphate media a chelated intermediate is postulated. Simultaneous Mn(III)/Mn(IV)-mediated reaction is observed in the oxidation of formaldehyde by

aquamanganese(III) ions.[40] The kinetics of the oxidation of neutral amino acids by manganese(III) ions in pyrophosphate solution have been studied.[41]

Electronic effects modulate *ee* in salen–Mn(III) alkene epoxidations. As a result of an excellent study, it has been suggested by Jacobsen and co-workers that more electron-donating substituents stabilize the Mn(V)oxo species relative to the Mn(IV) radical intermediate resulting in a later, more product-like transition state which gives greater enantioselectivity.[42] This suggestion was convincingly supported by linear Hammett plots of enantioselectivity versus σ_p and secondary isotope effects correlating k_H/k_D at C_β with enantioselectivity. Interestingly, Jacobsen and co-workers comment that the importance of transition state timing 'is quite reasonable in retrospect, but it could hardly have been anticipated in the initial design of these systems.' The generality of this discovery is that it might be usefully extended to many systems that, like Mn(III) epoxidations, do not involve substrate pre-arrangement. Mn(III), Co(II), and Ni(II)-salen complexes based on Schiff bases of (+)- or (−)-1,2-diamino-1,2-diphenylethane and benzaldehydes catalysed the asymmetric epoxidation of styrene by sodium hypochlorite.[43]

Oxidation of L-alanine by alkaline permanganate is first order in [permanganate] and fractional order in [L-alanine] and [alkali]. The proposed mechanism involves oxidation via two paths: the slow oxidation of L-alanine by permanganate to yield products and reaction of alkali and permanganate ion to give manganate.[44] A kinetic study of the oxidation of DL-alanine by acidic permanganate catalysed by silver(I) ion indicates a mechanism involving a rate-determining proton abstraction by water.[45] The kinetics of oxidation of alkyl cinnamates[46] using acetyltrimethylammonium permanganate have been studied and a mechanism involving a cyclic manganate(V) diester intermediate is proposed. Investigation of the kinetics of the oxidation of benzene and alkylbenzenes by permanganate in aqueous perchloric acid solution has indicated that the MnO_3^+ species attacks the aromatic ring.[47] The oxidation of dimethyl and diphenyl sulfoxides by MnO_4^- in aqueous acetic acid has been found to be first order in [substrate] and [MnO_4^-].[48] Permanganate oxidizes benzyl alcohols and ethers to benzaldehyde and benzoate esters, respectively. In both cases, the rates respond in an identical way to substitution in the ring, suggesting that oxidation proceeds by the same mechanism.[49] The proposed mechanism involves an initial interaction between the HOMO of the reductant (oxygen $2p$ orbital) with the LUMO of the oxidant (manganese two-electron antibonding orbital), followed by rate-limiting hydrogen transfer. Under strongly alkaline conditions (pH>12), the stable reduction product of permanganate ion is the manganate ion MnO_4^{2-}.[50] The oxidation of mandelic acid by permanganate has been investigated under these conditions, revealing a stoichiometry of 1:2. Kinetic data suggest that an alkali–metal permanganate complex, formed in an initial equilibrium, reacts with the substrate to give another complex, $[PhCH(OH)C(O)O-Mn(=O)_2O_2]^{2-}$, which decomposes in a slow step with loss of CO_2 to give a free-radical intermediate $PhCH(OH)^\bullet$, corresponding to decarboxylated mandelic acid. This reacts with hydroxide ion and a second equivalent of permanganate to yield the final product, benzaldehyde. Oxidation of L-phenylalanine by alkaline permanganate proceeds via the formation of a complex between L-phenylalanine and

permanganate, which decomposes to the free radical of L-phenylalanine which reacts with another molecule of permanganate.[51]

A good fit between previously observed linear free Hammett plots and those based on a simple 3 + 2 FMO-based calculation fit well and therefore support a 3 + 2 mechanism for the addition of permanganate to a C=C double bond.[52] A scaling factor allowed the lateness or earliness of the transition state to be adjusted, and thus allowed adjustments that are consistent with the ability of MnO_4^{2-} to dihydroxylate both electron-rich and electron-poor alkenes.

Phenylhydrazones were oxidized by NiO_2 at 0 °C via a radical mechanism to afford C−C and C−N dimers.[53]

Silver, Copper, and Gold

The oxidation of 2-carboxyphenylacetic acid by peroxodisulfate ion is catalysed by Ag(I).[54] The kinetics of the oxidation of tetrahydrofurfuryl alcohol by ditelluratocuprate(III)[55] and by ditelluratoargentate(III)[56] in alkaline media have been studied.

The kinetics of the oxidation of isopropylamine by diperiodatocuprate(III) complex ion have been studied and the results are consistent with a mechanism in which dissociation of one of the periodate ligands is followed by an adduct formation between $[Cu(HIO_6)]^-$ and isopropylamine. Polymerization of acrylamide indicated the participation of free radicals.[57] The kinetics of the oxidation of several diols by diperiodatocuprate(III) (DPC) in aqueous alkaline media have been studied.[58]

The oxidation of glycolaldehyde by tetrachloroaurate[59] was carried out in acetic acid–sodium acetate buffer and found to be first order in [Au(III)] and [glycolaldehyde]. H^+ and Cl^- both retarded the reaction. A compatible mechanism was proposed, which involves a one-step, rate-determining, two-electron transfer and the involvement of three gold species, $AuCl_4^-$, $AuCl_3(OH_2)$, and $AuCl_3(OH)^-$, the last being the most active.

Cerium, Titanium, Cobalt, Vanadium, Tungsten, Rhenium, Palladium, Platinum, and Iridium

Homogeneous oxidations of alkanes by electrophilic late transition metals have been reviewed.[60]

The CO_2/Ce(IV) stoichiometry in Ce(IV) oxidation of 10 organic acids has been measured under aerobic and anaerobic conditions.[61] The various results are explained by possible mechanisms in which the initially formed radical either (i) recombines giving no CO_2, (ii) recombines giving an unstable product from which either one or two molecules of CO_2 splits off, giving a stoichiometry of 0.5 or 1, (iii) loses CO_2 itself giving a stoichiometry of 1, or (iv) under aerobic conditions, adds O_2 followed by combination of two peroxy radicals giving either zero or one molecule of CO_2 and a stoichiometry of zero or 0.5. The mechanism of the oxidation of anisole derivatives by Ce(IV) in $HClO_4$ solution has been reviewed.[62] Calculations of the electron and spin densities of corresponding radicals and radical cations have been used to discuss the oxidation of tetrafluorobenzene derivatives with cerium(IV) perchlorate.[63] A single-electron transfer is proposed in the oxidation of α-amino-4-imidazolepropionic acid

by cerium(IV) perchlorate.[64] The oxidation of the amino-acids Asp, Phe, and Ser by Ce(IV) to aldehydes, NH_3, and CO_2 is pseudo-first order whereas the oxidation of Met is second order.[65] The kinetics of the oxidation of benzyl alcohol to benzaldehyde by ceric sulfate have been studied.[66]

Non-linear effects (NLEs) between *ee* of reagent or ligand and product *ee* indicate the differential participation or non-participation of diastereomeric species.[67] Kagan and co-workers have suggested these as potential fingerprints of asymmetric processes using the example of asymmetric sulfoxidation by $Ti(i\text{-}PrO)_4$–tartrate–peroxide systems to highlight remarkable complexity in observed NLEs even with minor system modifications.[67] Asymmetric oxidations of alkyl azaheterocyclic sulfides using a TADDOL system incorporating a 1,4-diol ligand, titanium tetraisopropoxide, and *t*-butyl hydroperoxide give sulfoxides which are moderately enriched in the *S*-enantiomer.[68] The system displays linear chiral induction, suggesting an active species that contains only one TADDOL ligand. A model is proposed for the intermediate in which the peroxide is chelated to titanium and the substrate is axially bound such that the terminal peroxy oxygen, the titanium and the sulfur are coplanar. Titanium-catalysed, asymmetric sulfoxidation of alkyl aryl sulfides with chiral hydroperoxides has been studied, with (*S*)-(−)-1-phenylethylhydroperoxide being most effective.[69] Detailed mechanistic studies showed that the enantioselectivity results from a combination of a low selectivity (*ee* <20%) induction and then kinetic resolution (*ee* 80–85%) of the sulfoxide to sulfone. The over-oxidation (and better stereoselectivity) is attributed to preferential sulfoxide coordination to titanium.

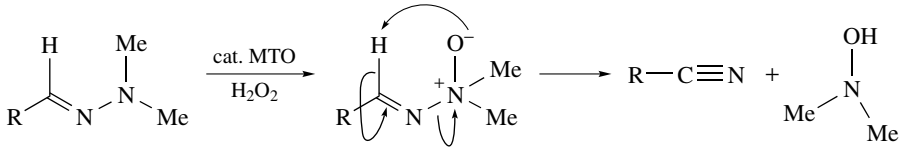
The oxidation of thioglycolic, thiomalic, and thiolactic acids in DMSO is first-order in tetrabutylammonium-12-tungstocobaltate(III) ion.[70]

The first example of the catalytic asymmetric oxidation of *t*-butyl disulfide to thiosulfinate has been described.[71] The use of a chiral Schiff base ligand, stoichiometric H_2O_2, and 0.25 mol% $VO(acac)_2$ gave the product in 91% *ee* and 92% yield. Good nucleophiles displace the *t*-BuS in the thiosulfinate with inversion of configuration as a ready route to various enantio-rich sulfinyl compounds. The oxidation of tartaric acid by vanadium(V), with and without control of ionic strength, has been investigated and a mechanism proposed for both cases. Comparison with published data on maleic and tartaric acid reveal that electron-withdrawing groups at the α-position of the substrate increase the oxidation rate.[72] A high negative ρ value (−3.64) was obtained in the oxidation of (phenylthio)acetic acids by vanadium(V) to corresponding diphenyl disulfide.[73]

The kinetics of the catalytic oxidation of cyclopentene to glutaraldehyde by aqueous hydrogen peroxide and tungstic acid have been studied and a compatible mechanism was proposed, which proceeds via cyclopentene oxide and β-hydroxycyclopentenyl hydroperoxide.[74] Monosubstituted heteropolytungstate-catalysed oxidation of alkenes by *t*-butyl hydroperoxide, iodosobenzene, and dioxygen have been studied; a radical mechanism was proved for the reaction of alkenes with *t*-BuOOH and O_2, but alkene epoxidation by iodosobenzene proceeds via oxidant coordination to the catalyst and has a heterolytic mechanism.[75]

Methyltrioxorhenium (MTO) is now well established as a catalyst in a number of oxidations employing hydrogen peroxide. Two groups have now reported,

independently, that this combination can be used for the oxidative transformation of *N*,*N*-dimethylhydrazones derived from aldehydes into nitriles.[76,77] The reaction has wide scope (aliphatic, unsaturated, aromatic, and heterocyclic aldehydes have all been used successfully), proceeds in high yields, and is selective over epoxidation of C=C bonds elsewhere in the substrate. It is suggested that the oxidation proceeds via the *N*-oxide (Scheme 2) which undergoes a Cope-type elimination of dimethylhydroxylamine to generate the nitrile. The former is further oxidized by a second equivalent of H_2O_2 to generate a nitrone, which has been detected by NMR. Stankovic and Espenson[76] reported that the optimum medium is acetonitrile–acetic acid–pyridine (94.5:5:0.5), the acid purportedly required to inhibit deactivation of MTO to perrhenate, and the pyridine to prevent hydrolysis to the parent aldehyde. However, Rudler and Denise[77] obtained comparable yields using ethanol alone as the solvent.



MTO = MeRe(=O)$_3$

SCHEME 2

Cerium(IV) oxidations of organic substrates are often catalysed by transition metal ions. The oxidation of formaldehyde to formic acid by cerium(IV) has been shown to be catalysed by iridium(III).[78] The observed kinetics can be explained in terms of an outer-sphere association of the oxidant, substrate, and catalyst in a pre-equilibrium, followed by electron transfer, to generate $Ce^{III}(S)Ir^{IV}$, where S is the hydrated form of formaldehyde $H_2C(OH)_2$. This is followed by electron transfer from S to Ir(IV) and loss of H^+ to generate the $H_2C(OH)O^{\bullet}$ radical, which is then oxidized by Ce(IV) in a fast step to the products. Ir(III) catalyses the *N*-bromobenzamide oxidation of mandelic acid[79] and *N*-bromosuccinimide oxidation of cycloheptanol in acidic solutions.[80]

The aerobic oxidation of terminal alkenes to alkan-2-ones is normally catalysed by an aqueous solution of palladium(II) and copper(II) salts under Wacker conditions. The copper(II) serves to mediate the re-oxidation of Pd(0) to Pd(II); addition of HCl is also necessary to inhibit clustering of atomic palladium, but this has drawbacks including reduction of catalytic activity, formation of chlorinated by-products and isomerization in the case of higher alkenes. Sheldon and co-workers, as part of a series of investigations of catalytic conversions in water, have shown that water-soluble palladium complexes with chelating diamines are able to catalyse such reactions efficiently, without the need for copper ions, chloride ions, or an organic solvent.[81] Bathophenanthroline disulfonate as ligand gave the best results; for example, hex-1-ene underwent 48% conversion into hexan-2-one in >99% selectivity. The catalyst could be recycled with only modest loss of activity, provided that sodium acetate was added, the role of which is probably to inhibit the formation of palladium clusters. Palladium(II) has been found to catalyse the oxidation of allyl alcohol by alkaline periodate.[82] The rate

increased upon addition of chloride ions, and the kinetic data were interpreted in terms of complex formation between the catalyst and substrate. The complex is oxidised by $H_2IO_6^{3-}$ in a rate-determining step to generate the $CH_2{=}CH\dot{C}HOH$ radical, which is then oxidized in a fast step to the product acrolein. It is proposed that the complex is a four-coordinate π-complex, in which the allyl alcohol acts as a bidentate ligand to palladium, binding through the alcohol and via the C=C double bond, the remaining sites being occupied by chloride and OH.

In the oxidation of glycolaldehyde in alkali, a two-electron-transfer process is proposed for Pt(IV) but a one-electron-transfer process for Ir(IV).[83]

Group VIII Metals

The mechanistic distinction between the iron–*t*-butyl hydroperoxide (TBHP) and the so-called Gif systems (iron salts and hydrogen peroxide) lies in the solely radical nature of the former, whereas in the Gif system, after initial formation of a carbon–iron bond, two manifolds exist, one involving Fe(III)–Fe(V) in which no radical is formed and the other involving Fe(II)–Fe(IV) in which fragmentation of the Fe(IV) species may give Fe(III) and a carbon radical in some cases. In radical chemistry, cyclooctane is more reactive than cyclohexane, while the reverse is true in Gif reactions. Furthermore, in Gif chemistry, saturated hydrocarbons are oxidized in the presence of alcohols without significant reaction of the latter. Competitive oxidations involving combinations of the above cycloalkanes and cyclooctanol, cyclohexanol, or 3-pentanol reveal product ratios consistent with a mechanism for the Gif reaction in which there is no initiation by oxygen radicals.[84] A review of Gif chemistry in 1998 by the late Sir Derek Barton, the originator, reinforces these conclusions.[85] The key observation is that the selective oxidation of saturated hydrocarbons in the presence of reductants such as H_2S or PhSeH is not compatible with radical chemistry, as has been suggested by others.

The Belusov–Zhabotinsky (BZ) reaction is catalyzed by a different mechanism when low-reduction-potential couples such as $[Fe(phen)_3]^{3+}/[Fe(phen)_3]^{2+}$ are employed. Experimental results for the BZ reaction with this couple in aerated conditions are compared with satisfactory agreement to a model calculation based on an 18-step skeleton mechanism, which includes reactions of organic radicals and molecular oxygen.[86]

Various metallo-phthalocyanines (Pht) and metallo-tetraphenylporphyrins (TTP) have been tested as catalysts for the oxidation of sulfides into sulfones by hydrogen peroxide.[87] TPPFe(III)Cl in ethanol was the only catalyst tested to give 100% conversion into sulfones in under 5 min; sulfoxides were identified as intermediates. PhtFe(III) gave sulfoxides in 100% yield and PhtMn(III) and TPPMn(III)Cl gave the sulfoxides in up to 70% yields. The absence of any by-product, in particular disulfide, suggests that a sulfenium radical cation is not an active intermediate in this process. The active metallic species is thought to be the oxene, $Por{-}\overset{+\bullet}{M}{=}O$; the mechanism is discussed in terms of the competing reactions of this species and the superior performance of the Fe(III) over the Mn(III) system is attributed to the faster oxygen transfer from the oxene to the sulfide or sulfoxide.

The oxidative behaviour of glycolaldehyde towards hexacyanoferrate(III) in alkaline media has been investigated and a mechanism proposed, which involves an intermediate alkoxide ion.[88] Reactions of tetranitromethane with the luminol and luminol-peroxide radical anions have been shown to contribute substantially to the tetranitromethane reduction in luminol oxidation with hexacyanoferrate(III) in aerated aqueous alkali solutions.[89] The retarding effect of crown ethers on the oxidation of triethylamine by hexacyanoferrate(III) ion has been noted.[90] The influence of ionic strength on the rate constant of oxidation of ascorbic acid by hexacyanoferrate(III) in acidic media has been investigated.[91] The oxidations of CH_2=CHX (where X = CN, $CONH_2$, and CO_2^-) by alkaline hexacyanoferrate(III) to diols have been studied.[92]

The kinetics of the oxidation of 1,4-thioxane by potassium ferrate have been studied and a mechanism involving the reaction of thioxane and protonated ferrate as the rate-determining step is proposed.[93] An iron–carboxylate complex immobilized on a modified silica surface is able to catalyse the aerobic oxidation of hexane to a mixture of hexan-1-ol, -2-ol, and -3-ol, with no ketone formation.[94] Reaction does not proceed in the absence of a thiol (propane-1,3-dithiol) and yields and rates were greatly increased by added triphenylphosphine and acetic acid. A mechanism has been put forward in which reduction of Fe(III) to Fe(II) by the thiol initiates the reaction and the alkyl disulfide formed reacts with Ph_3P to form a thioalkoxyphosphonium cation intermediate. Oxygen-18 labelling studies suggest that this intermediate is attacked by a dioxygen–metal adduct to generate Ph_3PO and an iron-oxo species from which oxygen is transferred to the substrate. Parallels are drawn with reactions in cytochrome P-450 model studies.

Ruthenium(III) catalyses the oxidative decarboxylation of *n*-butyric acid and isobutyric acid by ceric sulfate in aqueous acid.[95] A mechanism for the Ru(III)-catalysed oxidation of *o*-hydroxybenzoic acid by an acidic solution of bromamine-B ($PhSO_2$-NNaBr, BAB) has been proposed based on a kinetic study.[96] An ionic mechanism is suggested for the ruthenium(III) analogue of the Udenfriend-type system Ru(III)–EDTA–ascorbate–O_2, for the selective oxygen-atom transfer to saturated and unsaturated hydrocarbons.[97] The kinetics of the oxidation of p-$XC_6H_4CHPhOH$(X = H, Cl, Br, NO_2, Me, MeO) by bromamine-B, catalysed in the presence of HCl in 30% aqueous methanol by $RuCl_3$ have been studied and a biphasic Hammett σ-relationship derived.[98] A kinetic study of the ruthenium(III)-catalysed oxidation of aliphatic primary amines by sodium *N*-bromo-*p*-toluenesulfonamide (bromamine-T, BAT) in hydrochloric acid medium has been undertaken and the mechanism of the reaction discussed.[99] A concerted hydrogen-atom transfer one-electron transfer mechanism is proposed for the ruthenium(III)-catalysed oxidation of 2-methylpentane-2,4-diol by alkaline hexacyanoferrate(III).[100] The kinetics of the oxidation of propane-1,3-diol under the same conditions have been studied.[101] Ruthenium(III) catalyses the oxidation of primary alcohols by bromamine-B. A Taft LFE reaction constant of $\rho^* = -0.77$ indicates the development of positive charge in the transition state.[102]

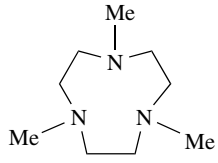
In the presence of ruthenium trichloride, alkaline sodium hypochlorite is able to oxidize methylbenzenes to benzoic acids under phase-transfer conditions at room temperature. In a recent development, selective oxidation of xylenes to toluic acids has

been achieved.[103] The selectivity for oxidation of just one of the two methyl groups lies in the fact that the monobenzoic acid, once formed, is immediately extracted into the aqueous phase. Electron-withdrawing substituents in the ring which have lone pairs of electrons (e.g. Cl or Br) direct the oxidation to the methyl group *ortho* or *para* to it, whereas for those with no unshared pairs of electrons (e.g. nitro, sulfonate, or carboxylate), the methyl group in the *meta* position is oxidised. This is rationalised in terms of the ability of the substituent to stabilise the carbocation formed by hydride abstraction from the substrate by RuO_4. Electron-donating substituents also favour ring chlorination.

A kinetic study of the oxidation of secondary alcohols by *N*-methylmorpholine-*N*-oxide (NMO) catalysed by the *trans*-dioxo-ruthenium(VI) complex, $[PPh_3(CH_2Ph)]^+[Ru(O)_2OAcCl_2]^-$, or tetrapropylammonium perruthenate indicates that the first step of the mechanism is the formation of a complex between the catalyst and substrate.[104] The oxidations of a series of benzydrols by *trans*-$[(TMC)Ru(VI)(O)_2]^{2+}$ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazocyclotetradecane) are correlated by a Hammett σ plot indicating that a carbocation-type intermediate is not involved. A primary deuterium isotope effect for the α-proton and absence of an O–D isotope effect suggest that α-C–H bond cleavage is rate-limiting. Two mechanisms are proposed:[105] one is a 2 + 2(C–H + Ru=O) addition involving an organometallic intermediate in which the new ligand is attached through carbon; the other involves the formation of an intermediate ruthenate ester, in which the oxygen-bound ligand undergoes a cyclic transfer of hydrogen to Ru=O, thereby being released from the metal. Molecular-orbital considerations favour the second theory.

A mechanistic investigation of four Schiff base–Ru(IV) complexes in asymmetric epoxidation has been conducted.[106] The observation of inverse kinetic isotope effects for the oxidation of β-d_2-styrene due to rehybridization and its absence in the α-deuteriostyrene oxidations discount a rate-limiting formation of a metallooxetane or a concerted oxene insertion mechanism. A linear-free-energy relationship between log k and total substituent effects for the ruthenium oxidation of *para*-substituted styrenes suggests a rate-limiting formation of a benzylic radical intermediate. Moderate enantioselectivities were observed because the acyclic carbon-centred radical intermediate undergoes collapse (*cis*) or rotation–collapse (*trans*) processes before the epoxide-forming ring closure.

Complex (**1**) is a catalyst for selective oxidation of benzylic, allylic alcohols to aldehydes, and secondary alcohols to ketones using *t*-butyl hydroperoxide.[107] Primary aliphatic alcohol oxidation failed. The use of cumyl hydroperoxide as radical probe discounted the involvement of *t*-BuO$^\bullet$/*t*-BuOO$^\bullet$. Hammett studies ($\rho = -0.47$) and kinetic isotope effects ($k_H/k_D = 4.8$) have been interpreted as suggesting an Ru–OO–Bu-*t* intermediate oxidant.



$Ru^{III}(CF_3CO_2^-)_3$

(**1**)

The kinetics of osmium(VIII)-catalysed oxidation of dimethyl sulfoxide by diperiodatonickelate(IV) in aqueous alkaline medium have been investigated.[108] Monoperiodatonickelate(IV) and $[OsO_4(OH)_2]^{2-}$ were the suggested active species of oxidant and catalyst, respectively. The kinetics of oxidation of cycloheptanol by hexacyanoferrate(III) in the presence of Os(VIII) have been investigated; a low [Os(VIII)] allows its continuous regeneration by hexacyanoferrate(III) ions.[109] Oxidation of propanal by potassium hexacyanoferrate(III) catalysed by osmium tetraoxide in alkaline media is zero order with respect to oxidant and first order with respect to catalyst.[110] The kinetics of the oxidation of reducing sugars by osmium tetraoxide in alkaline medium suggest the formation of an activated complex between enediol and osmium tetraoxide, which slowly disproportionates to give an osmium(VI) species and the intermediate products. Key changes are mainly due to the known Lobry de Bruyn–Van Ekenstein reaction.[111] Os(VIII) catalyses the oxidation of glutamic acid by chloramine-T.[112] In the oxidation of glycolaldehyde in alkali, a two-electron-transfer process is proposed for Os(VIII).[83]

Oxidation by Compounds of Non-Metallic Elements

Nitrogen, Sulfur, and Tellurium

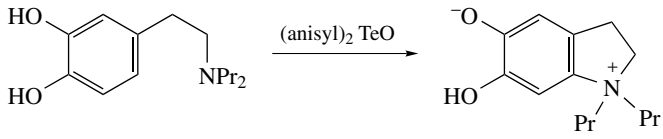
Many oxaziridines are oxidants. 2-*t*-Butyl-3-phenyloxaziridine, hitherto thought to be inactive as an oxidant owing to thermal rearrangement to *N*-*t*-butyl-α-phenyl nitrone, has now been shown to be effective in oxidizing sulfides to sulfoxides, provided that very high pressures are employed.[113] At 800 MPa, methyl phenyl sulfide was oxidized to methyl phenyl sulfoxide, the other major product being *N*-*t*-butylbenzaldimine (from the oxaziridine). At a lower pressure of 400 MPa, in contrast, the major product was *N*-*t*-butyl-α-phenyl nitrone. These results are interpreted in terms of competition between oxaziridine ring rearrangement and sulfide oxidation. Both processes release strain in the oxaziridine, but the latter requires the close approach of the two reactants, which is excessively hindered at all but very high pressures by the bulkiness of the substituents. Davis and co-workers have studied the oxidation of enolates of 1,3-dicarbonyl compounds using (camphorylsulfonyl)oxaziridine as a source of electrophilic oxygen to give an α-alkoxide that, upon work-up, gives an α-hydroxy product or undergoes Baeyer–Villiger-type rearrangement via the attack of O^- on the neighbouring C=O.[114] Only when the keto group was part of six-membered rings were useful *ee*s observed.

Nitrosoalkanes $Me_2C(CH_2X)NO$ are oxidized by NO_2 in CCl_4 much more rapidly than nitrosoarenes. Using stopped-flow techniques, Arrhenius parameters have been determined for several X substituents, revealing that electron-withdrawing substituents significantly decrease the rates, an observation that has been discussed in terms of the atomic charges at the nitrogen atom as calculated by the TNDO/2 method.[115] L-Ascorbate reduces substituted nitrosobenzenes giving the corresponding phenylhydroxylamines.[116] A Hammett σ^+ relationship and a primary kinetic deuterium isotope effect suggest that the reaction proceeds via a rate-determining cyclic transition state in which the transfer of the 2-H proton of ascorbate and the electron transfer from the anionic ascorbate oxygen are concerted.

Peroxynitrous acid, which has an estimated lifetime of 1–3 s at neutral pH, has been studied through *ab initio* calculations that suggest that peroxynitrous acid, peroxyformic acid, and dimethyldioxirane have, despite diverse O–O bond energies, similar activation energies for oxygen-atom transfer.[117] The transition-state structures for the epoxidation of ethene and propene with peroxynitrous acid are symmetrical with equal or almost equal bond distances between the spiro oxygen and the carbons of the double bond.

The kinetics of oxidation of several *para*-substituted anilines[118] and aliphatic acetals[119] by peroxomonosulfate in aqueous acetic acid have been investigated. In the oxidation of sulfides to sulfoxides by peroxymonosulfate (Oxone), the observed increase in second-order rate constants with increasing concentration of H_2SO_4 has been shown to be due to the increasing polarity of the medium, rather than to acid catalysis.[120] Similar conclusions were arrived at for the oxidation of aryl thiobenzoates and thiol-phosphorus(V) esters.

Dianisyltellurium oxide (DAT) is a mild and selective oxidant for quinone formation.[121] Treatment of the *N*,*N*-di-*n*-propyldopamine (**2**) with DAT leads to the betaine (**3**), which is identical with the product of oxidation by the enzyme tyrosinase both of (**2**) and of the monohydric phenol *N*,*N*-dimethyltyramine. The implications and relevance to the mode of action of tyrosinases have been discussed.



(**2**) (**3**)

Halogens

The oxidations of secondary alcohols and sulfides by halamine polymers produce ketones and sulfoxides, respectively, with some sulfones and chlorosulfoxides produced in the latter case. A mechanism is proposed based on the oxidation kinetics.[122] A review of the oxidation of haloalkanes with halogens and their derivatives has appeared.[123]

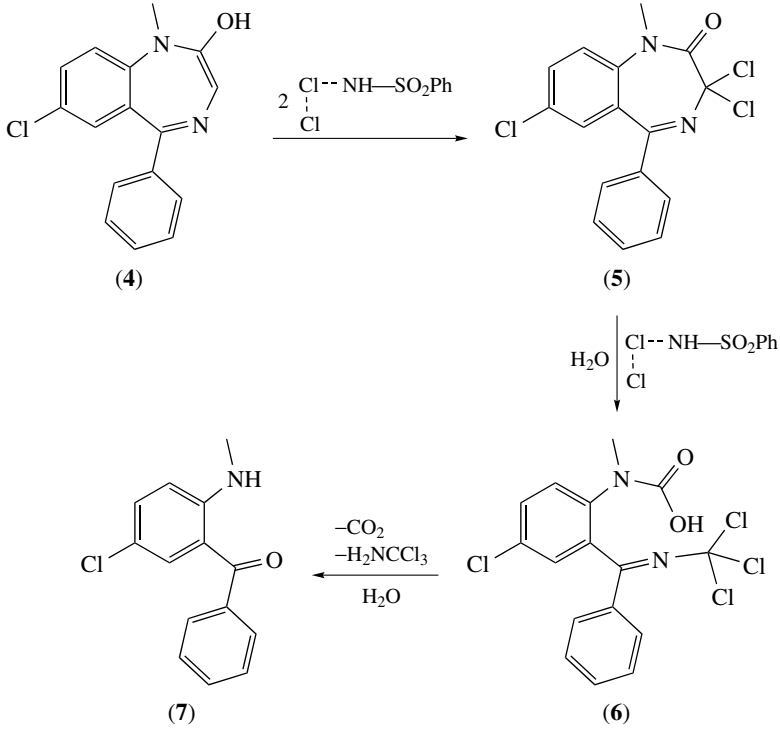
In the oxidation of aliphatic amines by aqueous chlorine, the key rate-limiting step is the transfer of chlorine from HOCl to the amino group N with probable involvement in the transition state of water molecules.[124]

The oxidation of formaldehyde by chlorite, ClO_2^-, has been studied in aqueous solution.[125] In the presence of excess chlorite, formaldehyde was oxidized to CO_2, with ClO_2 also being formed. This compound was also obtained as an oxidation product when HCHO was in excess, in which case the latter was oxidized only as far as formic acid. The first step of the reaction produces HOCl, which acts as an autocatalyst, catalysing the formation of ClO_2 and the further oxidation of HCO_2H to CO_2. The build-up of ClO_2 is due to the fact that HOCl reacts much more rapidly

with ClO_2^- than with the other reductants, and also to the relative unreactivity of ClO_2 towards HCHO and HCO_2H.

Kinetic studies on the oxidation of amino acids by chloramine-B (CAB, $PhSO_2NNaCl$) in acidic aqueous methanol reveals a dependence of the mechanism on the solvent composition and pH; a two-pathway mechanism is therefore proposed with substrate-dependent and independent paths.[126] The oxidation of diazepam by chloramine-B in aqueous hydrochloric acid medium was studied and found to exhibit first-order kinetics in the oxidant and fractional orders in HCl and diazepam. The overall reaction was found to involve a six-electron change. In acidic solution, chloramine-B exists in equilibrium between a variety of species; kinetic studies showed $PhSO_2NHCl$ to be the effective oxidizing species. A mechanism (Scheme 3) was proposed[127] in which $PhSO_2NHCl$ is protonated and forms an ion pair with chloride ion. This intermediate then reacts with the substrate in the enol form (**4**) giving an intermediate, which reacts with a second molecule of the oxidant to give the dichloro species (**5**). A final reaction of the oxidant with simultaneous hydrolysis gives (**6**) which, after decomposition in the presence of water, gives the product (5-chloro-2-methylaminophenyl)phenylmethanone (**7**).

It is suggested that oxidative degradation of D-mannosamine, D-galactosamine, and D-glucosamine by CAB involves attack of an anomeric alkoxide on CAB as a source of Cl^+ followed by elimination to lactone.[128]



The kinetics of the oxidation of metol [4-(methylamino)phenol sulfate] with chloramine-T (sodium *N*-chloro-*p*-toluenesulfonamide) have been studied, and possible mechanisms in which $ArSO_2NHCl$ was the reactive species have been discussed.[129] The kinetics of oxidation of some substituted piperidin-4-ols by chloramine-T have been studied and a compatible mechanism proposed.[130] The kinetics of oxidation of D-mannosamine by chloramine-T in alkaline medium are consistent with a stepwise mechanism in which the reaction of the enol-anion of the sugar with the oxidant is rate limiting.[131] A mechanism involving the aldo-enolic anions of pentoses and keto-enolic anions of hexoses is suggested for the oxidation of *erythro*-series pentoses and hexoses by chloramine-T.[132] Tetracyclines are oxidized by chloramine-T in aqueous acetic acid with concomitant decarboxylation.[133] The kinetics of oxidation of amino acids (leucine, serine, asparagine, glutamine, glutamic acid, and proline) by chloramine-T have been investigated.[134] The kinetics of chloramine-T oxidation of triethanolamine in alkaline media have been investigated.[135]

Mechanisms involving glycol bond fission have been proposed for the oxidation of vicinal diols, and hydride transfer for other diols in the oxidation of diols by bromine in acid solution.[136] The kinetics of oxidation of some five-ring heterocyclic aldehydes by acidic bromate have been studied.[137] The reaction of phenothiazin-5-ium 3-amino-7-dimethylamino-2-methyl chloride (toluidine blue) with acidic bromate has been studied.[138] Kinetic studies revealed an initial induction period before the rapid consumption of substrate and this is accounted for by a mechanism in which bromide ion is converted into the active bromate and hyperbromous acid during induction and the substrate is converted into the demethylated sulfoxide.

A primary kinetic isotope effect ($k_H/k_D = 6.03$ at 298 K) was observed for the oxidation of formic and oxalic acids by benzyltrimethylammonium tribromide (BTMAB) to carbon dioxide.[139] The kinetics of oxidation of pyridoxine to pyridoxal by bromamine-T and bromamine-B[140] and caffeine by bromamine-B[141] have been investigated.

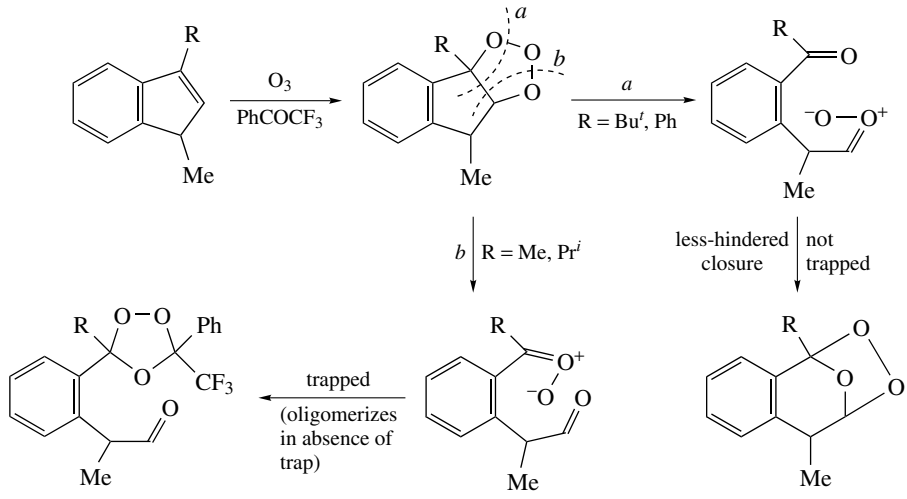
Kinetic studies of the oxidation of aspirin by bromamine-T, *N*-bromosuccinimide (NBS), and *N*-bromophthalimide (NBP) support a mechanism in which the unprotonated oxidant is the active species.[142] The ultimate product of the reaction is 2,4,6-tribromophenol, which arises through decarboxylation, bromination and loss of acetic acid. The NBP and NBS oxidations of α-hydroxy acids are found to be similar in mechanism.[143]

The effect of pH on the periodate oxidation of seven anilines has been investigated.[144] The kinetics of periodate oxidation of aromatic amines have been studied.[145,146] Periodate oxidation of oxalic acid is catalysed by Mn(II).[147] The reaction of ethane-1,2-diol with periodate has been investigated under a variety of conditions and the results compared with those of earlier work and analogous studies on pinacol.[148] The IO_4^- ion is the primary reactant, with H_5IO_6 as a secondary reactant; the reverse is true for pinacol. The complex observed in previous work is shown not to be an intermediate, but rather to deactivate the reactants.

Ozonolysis and Ozonation

Solvent effects on relative stability and electronic and molecular structure of carbonyl oxide (Criegee) intermediates in ozonolysis have been analysed by *ab initio*

calculations and revealed that stability was enhanced by favouring the zwitterionic form of carbonyl oxide.[149] A theoretical study of the electronic structures of oxygenated dipoles in relation to concerted and biradical mechanisms of 1,3-dipolar additions and ozonolyses in the gas phase has been published.[150] Ozonolyses of 3-alkyl-substituted 1-methylindenes and cyclopentenes suggest that collapse of the primary ozonide is influenced by the bulk of the substituent R (Scheme 3).[151] The nature of the resulting carbonyl oxide–carbonyl pair then influences the success of secondary ozonide formation.



SCHEME 3

Ozonolysis of styrene and ethylidenecyclohexane in the presence of [^{17}O]benzaldehyde yields stable secondary ozonides incorporating ^{17}O. ^{17}O NMR showed that labelled oxygen appeared as the ether oxygen, not the peroxo bridge, thus confirming the Criegee mechanism as opposed to the so-called unified concept.[152]

Gas-phase oxidations by ozone are important in atmospheric chemistry. A detailed study of the ozone oxidation of ethene at atmospheric pressure has been carried out using FTIR spectroscopy to monitor product formation and reactions of the Criegee intermediate, in the presence of hydroxy and carbonyl compounds.[153] A detailed kinetic analysis for reaction of 2,3-dimethylbut-2-ene has also been reported.[154] The mechanism of ozonolysis of methyl vinyl ketone, methacrolein, methacrylic acid, and acrylic acid in the gas phase have been investigated, and in particular the fate of the Criegee intermediate or carbonyl oxide was addressed.[155] Rate constants for the gas-phase ozonolysis of a range of unsaturated oxygenates were measured and compared with literature data. The results were discussed in terms of reactivity towards ozone as a function of the nature, number, and position of oxygen-containing substituents.[156] OH radicals were detected in reactions of ozone with alkenes in the gas phase by the use of hydrocarbon OH 'tracer' compounds.[157]

Ozone also reacts with *ethane* in the gas phase at room temperature. Rather than a direct molecular reaction, however, evidence points to the initiation of radical-chain reactions by the very small O-atom concentrations present in ozone at room temperature.[158] Added oxygen scavenges the radicals and slows the build-up, leading to induction periods which may be in excess of 3 h. Recent advances in mechanistic investigations of gas-phase ozonolysis of alkanes have been reviewed.[159] Oligomeric peroxides dominate the products of oxidation of nitrotoluenes with ozone in acetic acid.[160]

Peracids and Peroxides

Peracids *m*-CPBA and CF_3CO_3H have been used in epoxidations of substrates with two tunable allylic directing groups expected to direct the peracids to opposite faces of the alkene. Control of face selectivity was observed and attributed to the different binding abilities of the two peracids to the various allylic functionalities, carbamate on one side of the alkene and alcohol, methyl ester, acetate, trifluoroacetate, or TBS-ether on the other.[161] The conversion of *N*-mono-protected and *N*-di-protected cyclopent-3-enylamines to corresponding cyclopentene oxides using *m*-CPBA gave *cis*-epoxides and *trans*-epoxides, respectively. Amines protected with sterically small sulfonamides and carbamates gave the best *cis* selectivity; this is explained by hydrogen bonding between the *m*-CPBA and the NH for *N*-mono-protected amines, whereas *trans*-epoxides result from purely steric effects.[162] *Ab initio* calculations for the epoxidation of allyl alcohols with peroxyformic acid have revealed that the directing effect of the hydroxyl group is due to hydrogen bonding between the carbonyl oxygen of the peroxy acid and the allylic OH.[163]

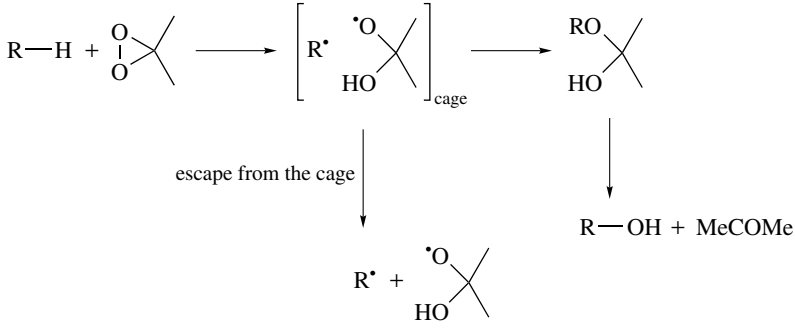
The oxidation of sulfoxides by aliphatic peroxy acids is first order in both reactants; the solvent effects have also been investigated.[164] Thiosulfinates are oxidized by peroxy acids to thiosulfonates and not disulfoxides. It had previously been proposed that the disulfoxides are formed first but homolytically cleave and recombine to give thiosulfonates. A series of *ab initio* calculations were performed (at the 3–21G* and 6–31G* levels) which indicate little difference in the rate of oxidation of S over S(O) in the gas phase but faster S(O) oxidation in a reaction cluster.[165]

The use and investigation of dioxiranes continues to expand rapidly. In low-conversion mono-epoxidations of allylic alcohols with (trifluoromethyl)methyldioxirane (TFDO) and dimethyldioxirane (DMDO), the less nucleophilic 2,3-double bond of geraniol is rendered more reactive by a hydrogen-bond-stabilized transition state when less polar aprotic solvents are used, although the effect is more pronounced with DMDO.[166] In chiral allylic alcohols, intramolecular hydrogen bonding controls the diastereoselectivity. In TFDO epoxidations of cyclic allylic alcohols, no enone formation is seen, as it is with DMDO. Kinetic data for the epoxidation of *cis*-alkenes and cycloalkenes with DMDO in acetone are consistent with a mechanism involving a spiro transition state.[167] DFT at the B3LYP/6–31 G* level, using a model solvent dielectric $\varepsilon = 20$, for the DMDO-mediated epoxidation of 2-methylbut-2-ene allowed enthalpies of activation to be calculated similar to those determined experimentally in acetone.[168] The system also showed substantially decreased activation barriers

when hydrogen-bonding substituents were present due to hydrogen bonding and not due to inductive effects. An even more significant lowering was observed when hydrogen bonding to methanol as a model protic solvent and this can understandably account for lowered selectivities in such solvents. 6–31 G*-level calculations for alkene epoxidation using dioxiranes predict a symmetrical spiro-butterfly transition state with two identical C—O forming bond lengths[169] and support hydrogen-bonding interactions (<25 kJ mol^{-1}) in the epoxidations of allylic alcohols with dioxiranes.[170]

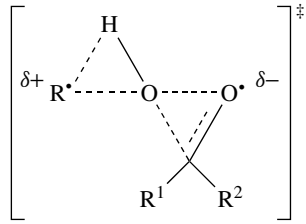
In situ-generated *N*-oxides have been shown to react with DMDO or TFDO reverting to the corresponding amines and singlet oxygen, $^1O_2$. In the case of nucleophilic, heteroaromatic *N*-oxides, the decomposition of the dioxirane by the *N*-oxide is slow compared with the oxidation, and the *N*-oxide predominates.[171] As discussed in *Organic Reaction Mechanisms 1997*, the mechanisms of many oxidations by dimethyldioxirane have been the subject of some controversy. Increasingly, evidence points to an electrophilic S_N2 mechanism (e.g. for epoxidation and alkene-insertion reactions), but other studies have suggested the involvement of bis(oxyl) radicals. The oxidation of a series of *N*,*N*-dimethylanilines by DMDO (to the *N*-oxides) has been investigated with respect to sensitivity to *para* substituents, and compared with analogous oxidations by *t*-butyl hydroperoxide (TBHP) (where a homolytic pathway is thought to be involved) and benzoyl peroxide (electrophilic mechanism).[172] Reactivity decreased in the order MeO > H > Cl > NO_2 for oxidations by DMDO and $(PhCOO)_2$, in line with an electrophilic mechanism, whereas the TBHP reactions were less susceptible to changes in substituent, as expected for a non-electrophilic reaction. Further analysis showed no evidence for free radicals or electron transfer in the DMDO oxidation.

Similarly, an interesting and somewhat controversial discourse has developed as to the mechanism of DMDO-mediated alkene oxidation: is it concerted oxygen insertion or radical? Although the former is more widely accepted, Minisci and co-workers have presented evidence that supports a radical mechanism.[173] Trapping products and the effect of oxygen suggested a molecule-induced homolysis of DMDO by alkanes, ethers, and aldehydes through hydrogen abstraction. The oxidation then occurs through cross-coupling of the radical pair in the solvent cage (rebound), while radicals escaping from the cage can initiate chains (Scheme 4). Less evidence exists for the subsequent suggestion by the authors that alkene epoxidation by analogy also proceeds in this way.



SCHEME 4

DMDO hydroxylation of a hypersensitive radical probe, *trans*-(2-ethylcyclopropyl)benzene, supports evidence for an oxygen-atom-insertion pathway over radical-pair formation.[174] Unrearranged and rearranged products are possible in this reaction, the latter arising from the ring opening of the radical formed by hydrogen abstraction from the cyclopropylcarbinyl position of the probe; a large predominance of unrearranged products was observed, indicating that the lifetime of the radical, if present, is too short for radical-pair formation. High-level *ab initio* calculations lend strong support to the generally accepted concerted electrophilic oxygen-insertion mechanism for the oxidation of alkanes to alcohols with dioxiranes under typical preparative conditions.[175] As part of this debate, *ab initio* calculations suggest a new mechanism of the dioxirane oxidation of aliphatic C−H bonds, which reconciles the apparently contradictory data.[176] A common transition state is suggested: the C−H bond is partially broken, the O−H bond is essentially completely formed, and the O−O bond is substantially broken (see structure). This is followed by either concerted transfer of the OH group to the carbon atom or separation into an α-hydroxyalkoxyl radical and an alkyl radical. These calculations reproduced the observed selectivity of the dioxirane oxidation of the C−H bonds in hydrocarbons, alcohols, and 1,2-diols. A very similar transition state was independently determined by Houk and co-workers.[177]

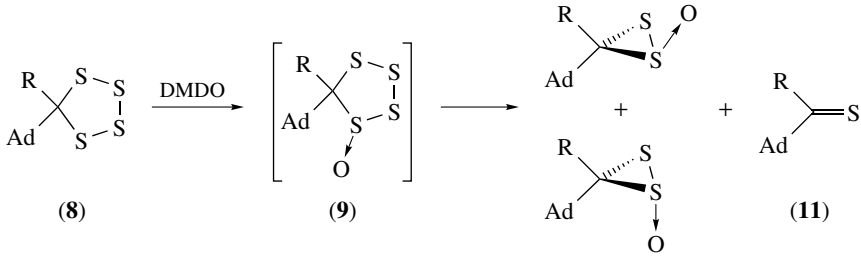


Kinetics of the dimethyldioxirane oxidation of adamantane in an oxygen atmosphere support a radical mechanism.[178] The kinetics of the oxidation of 2-methylbutane by DMDO in acetone solution have been studied and the mechanisms of the reaction and of inhibition of the reaction by O_2 were discussed.[179]

Oxidation of tetrathiolanes (**8**) with DMDO gave mixtures of dithiirane 1-oxides (**10**) and thioketones (**11**) (Scheme 5). The existence of the intermediate tetrathiolane 1-oxides (**9**) was verified by NMR of the cooled and evaporated reaction mixture.[180]

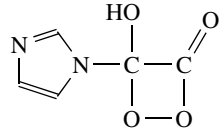
The relative reactivity of a wide series of nucleophiles towards dioxirane, dimethyldioxirane, carbonyl oxide, and dimethylcarbonyl oxide has been examined at various levels of theory.[181] The general trend in reactivity for oxidation by dioxirane was $R_2S \approx R_2SO$, $R_3P > R_3N$ in the gas phase, and $R_2S \approx R_2SO$, $R_3N \approx R_3P(R = Me)$ in solution. A theoretical study of the first oxidation step of [3.2.1]-bridged bicyclic disulfides highlights a highly oriented reaction path was probably responsible for stereoselective attack on the *exo* face.[182]

The existence of an intermediate species in the dioxygen transfer from 4a-hydroperoxyflavin anion to phenolate and indole anions has previously been shown and *ab initio* and semiempirical MO calculations have been used to examine possible candidates for



SCHEME 5

the intermediate;[183] two dioxetane species were identified as probable intermediates. Stopped-flow kinetics have been used to investigate the imidazole-catalysed peroxyoxalate chemiluminescence reaction of bis(2,4,6-trichlorophenyl) oxalate.[184] The failure of other amine bases suggests a role for imidazole as a nucleophilic catalyst. The results are consistent with an intermediate oxalyldiimidazole that reacts to form a monoperacid which in turn forms a high-energy light-generating intermediate (**12**).

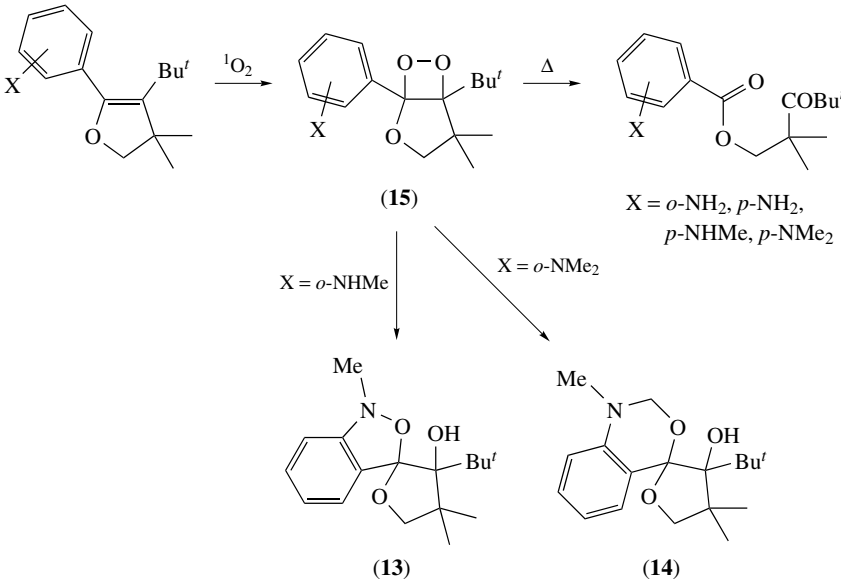


(**12**)

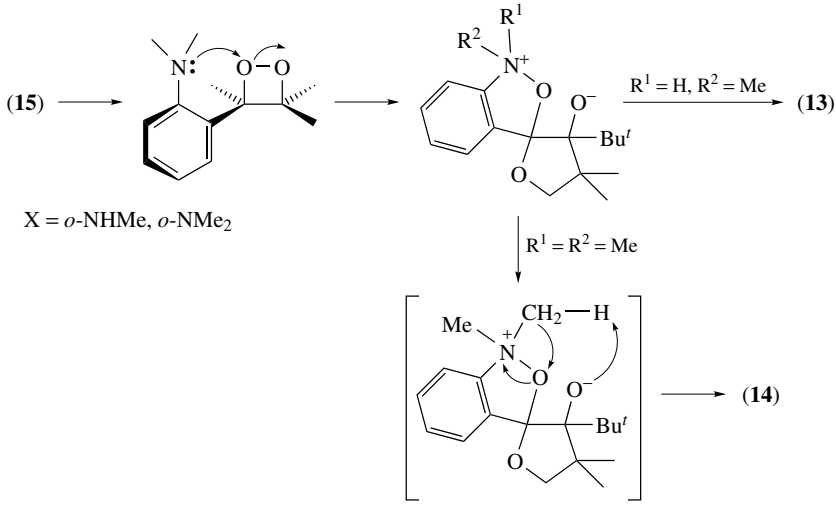
Although thermal decomposition of 1,2-dioxetanes normally leads to two carbonyl products, dioxetanes bearing a phenyl group substituted with an *N*-methylamino or *N*,*N*-dimethylamino group at the *ortho* position have been found to undergo a different and unusual decomposition pathway leading to heterocycles (**13**) and (**14**), despite the fact that the unsubstituted *o*- and *p*-amino analogues decompose in the normal fashion to carbonyl products (Scheme 6).[185] This interesting competitive pathway has been rationalized in terms of intramolecular nucleophilic attack of the *N*-methylamino group at the O−O moiety of the dioxetane and O−O bond fission, followed by proton exchange in the intermediate zwitterion (Scheme 7).

Hexamethylbenzene reacts with DMDO via three pathways: (i) to an arene oxide, which rapidly rearranges to an oxepin tautomer that then is oxidized to a *cis*-diepoxide and then to a *cis, cis,trans*-triepoxide; (ii) a methyl group migrates in the first epoxide to give a cyclohexadienone, which then reacts to give a *trans*-diepoxide; (iii) C−H insertion to give the benzyl alcohol and then the corresponding benzoic acid.[186]

Wang and Shi have published a detailed study of their fructose-based dioxirane epoxidation catalyst system with hydroxyalkene substrates.[187] The *ee*s obtained were highly pH dependent. The lower enantioselectivity obtained at low pH is attributed to the substantial contribution of direct epoxidation by Oxone. The results obtained with



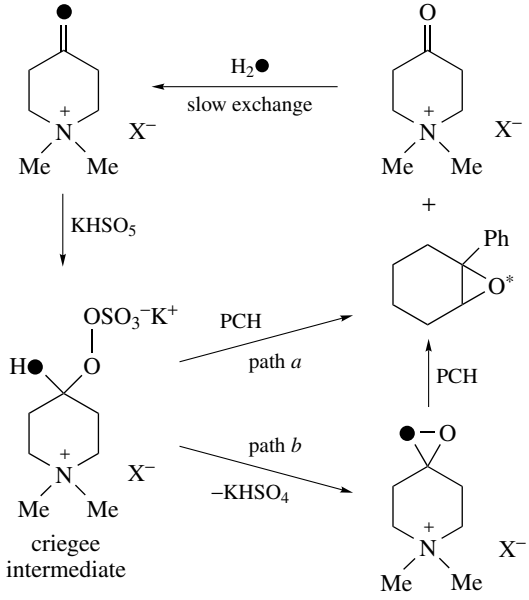
SCHEME 6



SCHEME 7

the corresponding TBS ethers strongly suggest that the epoxidation by Oxone was facilitated by the hydroxyl group in the substrate perhaps due to enhanced intramolecular epoxidation through hydrogen bonding or enhancing the aqueous solubility of the substrate.

Denmark and Wu have suggested[188] discrepancies in previous [^{18}O]dioxirane labelling experiments[189,190] and disclosed their results as shown in Scheme 8; 34% incorporation

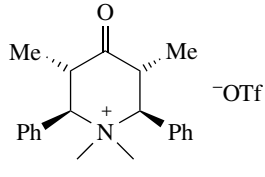


PCH = 1-phenylcyclohexene
● = ^{18}O (90% ^{18}O)
X = TfO

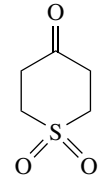
SCHEME 8

of ^{18}O into epoxide was observed. The disparity between 34% and the theoretically expected 43% (50% of the 86% present in the labelled water used) was attributed to the slow exchange of ketone O in $H_2{}^{18}O$. This was confirmed by increasing the number of ketone equivalents to 5, which gave increased (39%) incorporation. They suggest that the problem with previous ketone systems was that there was no mechanistically significant, ketone-catalysed pathway in those cases owing to the insolubility of the ketone in the aqueous phase, and that this explains the lack of ^{18}O incorporation observed in those previous cases.

By exploiting electrostatic field effects (unfavourable through-space charge–dipole repulsion) to increase the nucleophilic susceptibility of cyclohexanones, more efficient catalysts (**16**) and (**17**) for epoxidation through *in situ* dioxirane formation have been designed.[191]

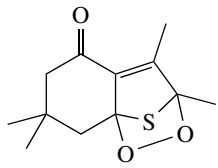


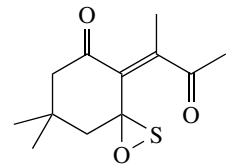
(**16**)

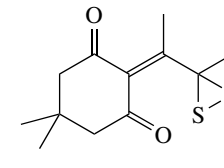


(**17**)

The thiophene endoperoxide (**18**) is a powerful episulfidation reagent.[192] The stereospecific transformation of *cis*- or *trans*-cyclooctene suggests a concerted process. First-order consumption kinetics have now shown that (**18**) is not itself the active *S*-transfer reagent: two such intermediates are proposed, possibly oxathiiranes such as (**19**) or (**20**), based on similarities in the trends for epoxidations of the same substrate by DMDO.[193]


(**18**)

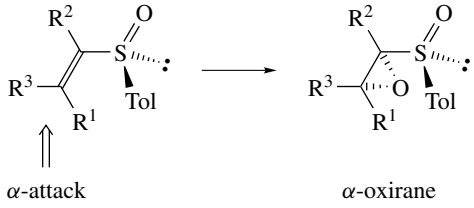

(**19**)


(**20**)

Pinene hydroperoxide (PHP) when compared with *t*-butyl hydroperoxide has been proposed as an excellent mechanistic probe in metal-catalysed oxidations.[194] If intermolecular oxygen transfer from a peroxometal species to the substrate is rate limiting, the bulky PHP is unreactive, but for reaction of an oxometal species as the rate-limiting step, little or no difference is observed and only small differences in reactivity are observed when re-oxidation of the catalyst by ROOH to an active oxometal species is the rate-limiting step.

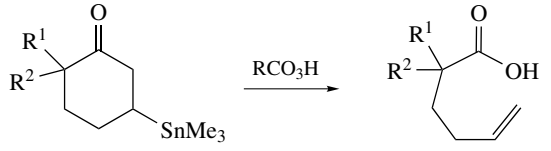
t-Butyl and cumene hydroperoxide allow hydroxylation of nitroarenes by vicarious nucleophilic substitution (nucleophilic addition of alkyl hydroperoxide anion followed by base-induced *E*2 β-elimination of ROH).[195] Stereoselective nucleophilic epoxidation of simple vinyl and dienyl sulfoxides with $NaOOBu^t$ or $KOOBu^t$ has been rationalized by initial nucleophilic addition to the α-face of the reactive conformation shown in Scheme 9 followed by epoxide ring closure.[196] It is likely that steric hindrance by the bulky tolyl group is a key factor. Interestingly, the diastereoselectivity of the epoxidation of (1*E*)-2-sulfinyl dienes can be altered by a simple change in the metal cation from Li^+ to Na^+.

Ab initio calculations of the transition-state energies in the epoxidation of alkenes by hydrogen peroxide catalysed by titanosilicates have been carried out.[197] They indicate a markedly lower energy barrier for attack of the alkene by the oxygen atom of the titanium(IV) hydroperoxide intermediate that is closer to the metal centre.



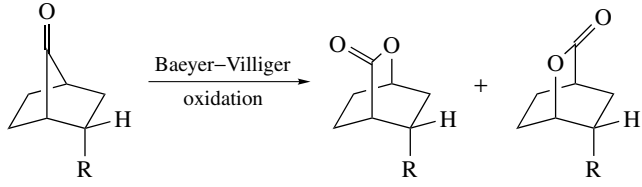
SCHEME 9

The Baeyer–Villiger (BV) oxidation of ketones to esters involves the migration of one of the groups flanking the carbonyl to the adjacent electron-deficient oxygen atom. For unsymmetrical ketones, the migratory aptitudes of the groups is determined by their relative abilities to support the developing positive charge in the transition state. It is well known that substituents of Group 14 (Si, Ge, and Sn) are able to stabilize positive charge at the β-position, and that a β-silicon atom does, indeed, enhance the migratory aptitude of groups in the BV reaction. A study of the BV reaction of β-stannyl cyclohexanones has now revealed that a β-trimethylstannyl substituent raises the migratory ability of a primary carbon to above that of a tertiary carbon (in the absence of other activation); thus, compounds (**21**)–(**23**) gave the acyclic alkene acids (**24**)–(**26**), either via the corresponding lactones or possibly a concerted breakdown of the initially formed tetrahedral intermediate.[198] A separate study on the BV oxidation of norbornan-7-ones has revealed a remarkable effect of distal 2-*endo*-substituents on migratory ability and hence on the regioselectivity of the reaction (Scheme 10).[199] Electron-withdrawing substituents at the C(2)-*endo* position reduce



(**21**) $R^1 = R^2 = H$
(**22**) $R^1 = H$, $R^2 = Me$
(**23**) $R^1 = R^2 = Me$

(**24**) $R^1 = R^2 = H$
(**25**) $R^1 = H$, $R^2 = Me$
(**26**) $R^1 = R^2 = Me$



A B

R	A:B product ratio
CN	100:0
CO_2Me	>90:10
OMe	77:23
Ph	51:49
C_6H_4OMe-*p*	39:61
OC_6H_4F-*p*	52:48
$C_6H_4NO_2$-*o*	70:30
$C_6H_4NO_2$-*p*	75:25

SCHEME 10

the propensity of the C(1)−C(7) bond to migrate compared with the C(4)−C(7); for R = CN, the effect is so large that migration of the latter occurs exclusively to give a single product. Thus, the strong inductive effect of such substituents is relayed to the C(1)−C(7) bond through the C(1)−C(2) bond. On the other hand, an aryl group at C(2) incorporating an electron-donating methoxy substituent leads to a reversal in regioselectivity. For a simple phenyl group (R = Ph), the inductive electron withdrawal is probably counterbalanced by through-space π-donation into the C(1)−C(2), leading to the absence of any migratory preference in this case.

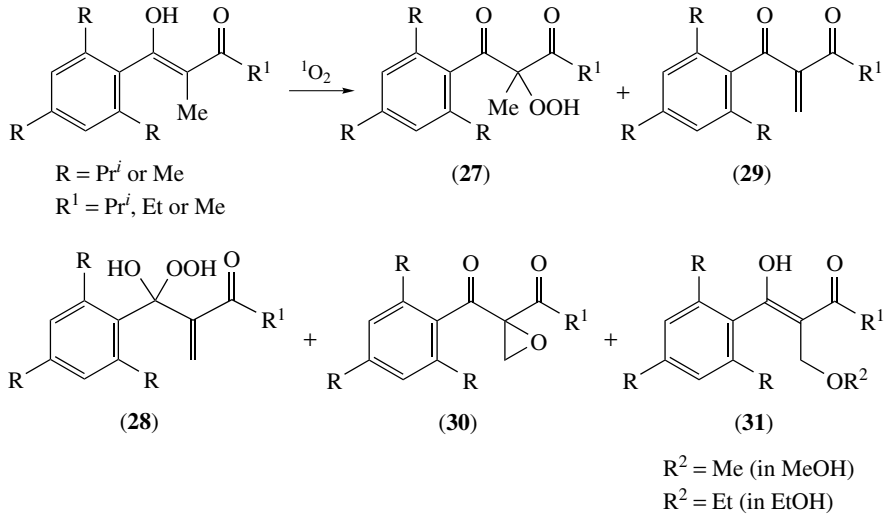
Some evidence for stereoelectronic effects in peroxide rearrangements, such as Criegee and Baeyer–Villiger rearrangements, has been determined.[200] Certain hydroperoxides display highly unusual reactivity patterns under conditions for effecting Criegee rearrangement. The bond conformation revealed in corresponding crystal structures suggests that the bond antiperiplanar to the dissociating peroxide bond is always and exclusively the bond that migrates, even when electronically disfavoured from doing so.

Fenton-type reagents [H_2O_2 or *t*-butyl hydroperoxide (TBHP) with Fe/Co/Cu catalysts] are of increasing interest as more benign, catalytic alternatives to the use of stoichiometric chromium-based oxidants in benzylic and allylic oxidations. In a study employing TBHP and copper salts under phase-transfer conditions, π-activated methylene groups are oxidized to *t*-butyl peroxides, e.g. 1,2,3,4-tetrahydronaphthalene (tetralin) is oxidized to 1-*t*-butylperoxytetralin.[201] The reaction proceeds according to a classic Kochi free-radical mechanism involving *t*-BuO radicals and Cu(II)−OOBu-*t*. Secondary allylic and benzylic alcohols are oxidized under the same conditions to ketones. In this case, however, observations including a very large kinetic isotope effect ($k_H/k_D = 12.9$) for PhCH(OH)Me compared with PhCD(OH)Me indicate that the rate-determining step involves breakage of the benzylic C−H bond and that reaction proceeds via a heterolytic mechanism, the copper catalyst being transformed to Cu(OH)Cl which enters the organic phase. The co-existence of two distinct reaction pathways in the same medium has been attributed to H-bonding of the alcohol substrate with the TBHP oxidant, which lessens the free-radical, peroxidic hydrogen abstraction by the *t*-butyloxy radical. A review on recent progress in the study of oxidation with hydrogen peroxide in organic synthesis has appeared.[202]

Photo-Oxygenation, Singlet Oxygen, and Superoxide

A type I one-electron photo-oxidation of methionine–methionine-containing peptides by triplet carboxybenzophenone in air-saturated aqueous solution has been reported; the $S^{+\bullet}$ radical cation that is formed then reacts with the other Met-S to form an S−S three-electron complex which reacts with superoxide radical anion before hydrolysis to Met(=O)−Met(=O) bis-sulfoxide.[203] Alternatively, cyclization of the *N*-terminal NH_2 on to the S can occur to give a three-electron S−N complex which can react with superoxide radical anion to give a cyclic sulfonium intermediate.

Whilst reactions of α,β-unsaturated carbonyl compounds with $^1O_2$ have been the subject of a number of studies, the corresponding reactions of their enolic tautomers have received little attention. Reaction of the β-hydroxy-α,β-unsaturated ketones

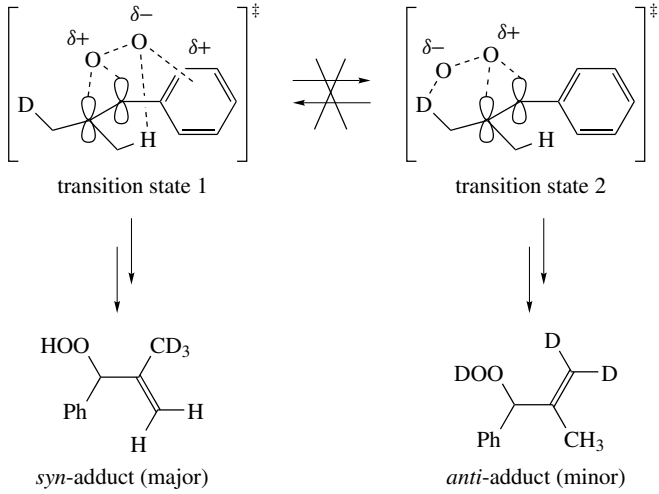


SCHEME 11

in Scheme 11 led to the products shown.[204] The photo-oxidation probably involves an ene reaction with $^1O_2$, in which the oxygen abstracts hydrogen either from the enolic hydroxy group, to generate (**27**), or from the 2-methyl group, leading to (**28**). Decomposition of (**28**) by loss of hydrogen peroxide leads to the major enedione product (**29**), which can subsequently react with the H_2O_2 liberated to give (**30**). In alcoholic solvents, compounds of the form (**31**) predominate, and are probably formed by conjugate addition of the alcohol on the enedione. Epoxidation to give (**30**) is reduced by bulky substituents in the ring *ortho* positions and at the terminal carbonyl, and favoured when all substituents are methyl. It has been shown that the phenyl ring of styrene substrates can dictate the *syn*/*anti* stereochemistry in ene reactions with singlet oxygen and triazolinediones, perhaps through a favourable interaction of the enophile with the phenyl ring (Scheme 12).[205]

Ab initio calculations of the transition structures for the Schenck reaction of singlet oxygen suggest that Me substitution makes the transition structure earlier and more stable and that the transition-state geometry is sensitive to the position of Me substituents.[206]

Tyrosine hydroxylase catalyses the formation of DOPA from tyrosine using molecular oxygen and tetrahydropterin as a co-factor. There are no primary deuterium or solvent kinetic isotope effects; however an ^{18}O isotope effect of 1.0175 ($\pm$0.0019) measured through the isolation of remaining O_2 has been recorded.[207] The results support a rate-limiting reductive activation of molecular oxygen via a one-electron transfer from the tetrahydropterin to from superoxide anion as a key reactive intermediate. *Ab initio* calculations suggest that an *S*-hydroperoxysulfonium ylid is an important intermediate in the $^1O_2$ oxidation of sulfides.[208] This ylid intermediate can rearrange to either an α-hydroperoxide or to a protonated sulfone ylid and then to the sulfone product. Similar results were obtained from an almost parallel study.[209]



SCHEME 12

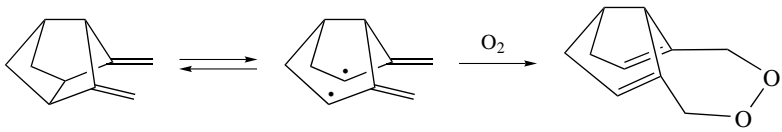
Atomic Oxygen, Triplet Oxygen, and Autoxidation

Under oxidative conditions, *p*-benzoquinone is primarily consumed via thermal dissociation at lower temperatures, whereas hydrogen-abstraction reactions with the O/H radical pool lead to OC_6H_3O and C_6H_3O at higher temperatures.[210] This shift occurs at lower temperatures with a higher oxygen concentration. The oxidation of isobutene in O_2 was studied in a continuous-flow stirred-tank reactor and shock tube.[211] Comparison of the partial-pressure profiles of various products of the reaction fit reasonably well with theoretical data obtained with CHEMKIN II software. The kinetics of the oxidation of dimethyl ether in a jet-stirred reactor and shock tube have been studied[212] and product and intermediate distributions compare well with calculations using a numerical model consisting of 336 reactions. The major products detected were CO, CO_2, H_2, H_2CO, and CH_4. The thermal gas-phase oxidation of tetrachloroethene by molecular oxygen in the presence of trifluoromethyl hypofluorite (CF_3OF) has been studied and a detailed mechanism was presented.[213] The application of a system of computer-aided design of kinetic models of oxidation and combustion to previously obtained results for the oxidation of *n*-octane and *n*-decane has been performed with satisfactory fitting of the conversion and distribution of products formed.[214] The oxidation of methanol over a wide range of temperature and pressure is sensitive to the kinetics of the hydroperoxyl radical through a branching mechanism involving hydrogen peroxide ($H_2O_2 \rightarrow 2OH$) at low temperature and a terminating mechanism ($H_2O_2 \rightarrow H_2O + O_2$) at high temperature.[215]

In order to model the oxygenation of vitamin K in its hydroquinone form, a naphthohydroquinone derivative with a 1-hydroxy group and 4-ethyl ether was prepared and its alkoxide subjected to oxidation with molecular oxygen.[216] Products consistent with two possible mechanisms were isolated, the epoxy-quinone which must derive from a peroxy anion intermediate at the 4-position, and a 2-hydroxy product which

could arise from a 2-peroxy anion intermediate. The liquid-phase oxidation of 1- and 2-isopropenylnaphthalene with pure oxygen in PhCl solution in the presence of cumene and cumene hydroperoxide at 75–125 °C has been investigated.[217]

The Cope rearrangement of the highly strained diene (**32**) (Scheme 13) is shown to proceed by a non-concerted mechanism involving the diradical (**33**), which may be trapped by oxygen to give the peroxide (**34**). A full kinetic study confirms the intermediacy of the diradical.[218]



(**32**) (**33**) (**34**)

SCHEME 13

The use of O(3P) atoms produced by microwave irradiation of He–O_2 mixtures has shown that alkenes react with atomic oxygen in solution or neat to give predominantly epoxides.[219] Unlike reactions in the gas phase, at low temperature these produce useful product yields and distributions. Similar yields suggest that epoxide formation and 1,2-H/1,2-C shifts/ring contractions compete.

Other Oxidations

The stereoselectivity of enzymatic primary carbon hydroxylation has been reviewed.[220] The phthalimide *N*-oxyl radical (PINO), which may be formed from *N*-hydroxyphthalimide (NHPI), has been shown to catalyse the oxygenation of alkynes to α, β-acetylenic ketones with dioxygen under mild conditions, in the presence of a transition metal catalyst, e.g. $Co(acac)_2$.[221] The subsequent introduction of oxygen into the prop-2-ynylic C–H bond is presumed to occur by a free-radical process involving hydrogen-atom abstraction at the energetically favourable prop-2-ynylic position. EPR analysis suggests that, in order for the PINO radical to be formed from NHPI, the alkynyl substrate must be present, in addition to O_2. The mechanism of the synergistic oxidation of cyclohexane with H_2S and O_2 has been investigated by addition of PhSeSePh; the results rule out the involvement of carbon and oxygen radicals.[222] The pyrolysis and oxidation of formaldehyde at high temperatures have been investigated by monitoring the progress of the reaction by laser absorption of CO molecules.[223] A detailed kinetic analysis led to a new reaction model giving good agreement with the experimental data.

Human type II inosine monophosphate dehydrogenase catalyses NAD-dependent conversion of inosine monophosphate (IMP) into xanthosine monophosphate (XMP); measurements of the primary kinetic isotope effect using [^{2}H]IMP suggest that both substrates (IMP and NAD) can dissociate from the enzyme–substrate complex; therefore, the kinetic mechanism is not ordered. NMR studies indicate hydride transfer to the B or *pro-S* face of the nicotinamide ring of NAD, while kinetic studies suggest

that this is a kinetically significant step, although the rate-limiting step occurs at a later stage in the mechanism.[224]

The one-electron oxidation of *N*-benzylphenothiazine by nitric acid occurs in the presence of β-cyclodextrin, which stabilizes the radical cation by incorporation into its cavity. The reaction is inhibited by adamantane, which preferentially occupies the cavity.[225] Novel Pummerer-type rearrangements of *p*-sulfinylphenyl derivatives, yielding *p*-quinones and protected dihydroquinones, and highly enantioselective Pummerer-type rearrangements of chiral, non-racemic sulfoxides have been reviewed.[226] A comprehensive study has demonstrated that the redox potential for 7- and 8-substituted flavins is linearly correlated with Hammett σ values.[227] DFT calculations in [3.3.*n*]propellanes highlight low ionization potentials that favour SET oxidative cleavage of the strained central C−C bond rather than direct C−H or C−C bond attack.[228] Oxidations and reductions in water have been reviewed.[229]

Reduction by Complex Metal Hydrides

The applications of sodium acyloxyborohydrides, formed from sodium borohydrides in carboxylic acid media, are reviewed.[230] Useful reviews of the stereoselective reduction of endocyclic C=N compounds[231] and of the enantioselective reduction of ketones have appeared.[232]

A nice analysis of non-linear effects in Rh−chiral diamine-catalysed transfer hydrogenation has been performed that reinforces the need to consider the kinetics of all of the steps in reaction manifolds (e.g. reversible formation of diastereomeric precursors and their subsequent interaction with achiral reactants).[233]

Some further examples of the reduction of adamantanones have highlighted that increasing the positive dipole on the C=O using Lewis acids, or placing charged substituents at C(5) within the adamantyl framework, enhances face selectivities in borohydride and aluminium hydride reductions due to Cieplak effects.[234]

Other Reductions

The reduction of (2,3)-α- and (2,3)-β-methylenepenam β-sulfoxides to the corresponding sulfides using potassium iodide and trifluoroacetic anhydride (TFAA) is found to be much faster than for bicyclic β-lactam β-sulfoxides.[235] In the proposed mechanism, initial attack of the sulfoxide oxygen on TFAA is followed by rate-limiting, nucleophilic displacement of trifluoroacetate by iodide ion; nucleophilic attack of iodide on the iodine atom then yields the sulfide and iodine. The rate enhancement is accounted for by the stabilization of the transition state in the rate-limiting step by interaction of the *p*-like orbital of sulfur and the cyclopropane σ^* orbital.

The results of kinetic studies on the reaction between iodide and *N*-chloro compounds support a mechanism in which the rate-determining transfer of Cl^+ from the *N*-chloramine to iodide gives an ICl intermediate which rapidly reacts with excess iodide to give triiodide ions.[236]

The mechanisms of electrochemical reduction of 9-chloroanthracene, 3-nitrobenzyl chloride, and 3-chloroacetophenone have been investigated by means of cyclic voltammetry.[237] The effect of different aprotic solvents was studied and, in the case of

9-chloroanthracene and 3-nitrobenzyl chloride, the rate of the reaction was found to depend on the electrophilic properties of the solvent as defined by Gutmann acceptor and donor numbers, respectively; 3-chloroacetophenone showed no linear dependence on solvent properties.

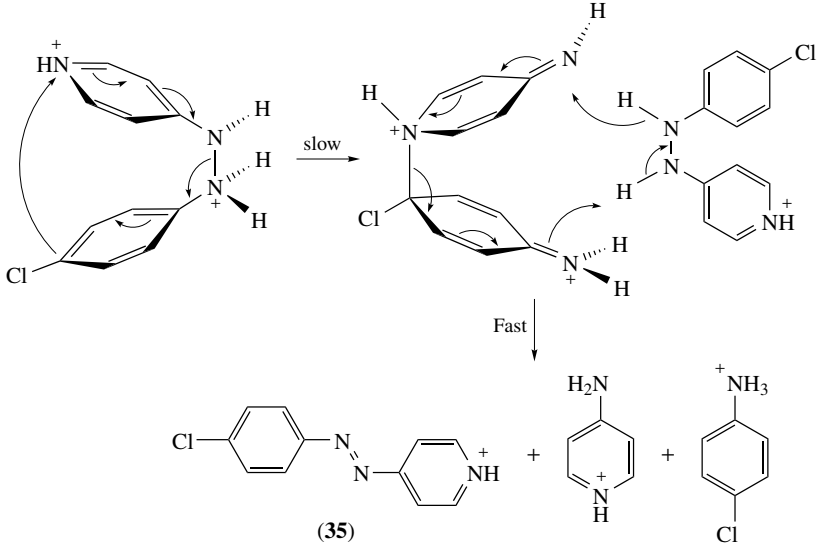
Atomic charges, effective charges at reacting centres, and HOMO and LUMO energies have been calculated for nitrobenzene, nitrosobenzene, *N*-phenylhydrazine, diphenyldiazine, *N*,*N*′-diphenyldiazine-*N*-oxide, and *N*,*N*′-diphenylhydrazine, compared with kinetic data for the hydrogenation of these compounds, and used to propose a mechanism for the hydrogenation of nitrobenzene.[238]

Reduction of *N*-arylmaleimides with sodium dithionate gives monomeric and dimeric products; a mechanism has been proposed.[239]

The kinetics of the reduction of 2,6-dichlorophenolindolphenol (DCPI), a common dye used for analysing ascorbic acid, by Fe^{2+} and oxalate have been studied and indicate the rapid formation of an intermediate complex of Fe^{2+} and $C_2O_4^{2-}$, predominantly FeC_2O_4, prior to the reduction of DCPI.[240]

Disproportionations

The disproportionation reactions of 4-(4-chlorophenylazo)pyridine and 4-(4-chlorophenylhydrazo)pyridine in acidic media have been studied. The hydrazo compound disproportionates to give 1 mol of the azo compound (**35**) and 1 mol each of the reduced products 4-chloroaniline and 4-aminopyridine. The azo compound also undergoes a slower hydroxylation reaction giving a variety of products. A proposed mechanism for the disproportionation of 4-(4-chlorophenylhydrazo)pyridine consistent with observed first-order kinetics involves a rate-determining electrocyclic rearrangement of the diprotonated species (Scheme 14).[241]



SCHEME 14

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