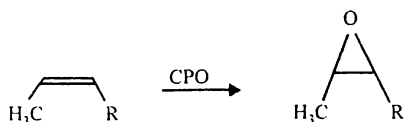


belong to the group of enzymes called as “Rieske oxygenases” which catalyses the *cis* hydroxylation of phthalate.

Phthalate dioxygenase represents the other *cis* dihydroxylating enzymes (Benzoate 1,2-dioxygenase, toluene 2,3-deoxygenase) that catalyse the initial step of degradation of aromatic rings, the dihydrodiol serves as the precursor to catechols that are cleaved by catechol dioxygenases.

Peroxidases

Peroxidases are of immense synthetic potential since they can in principle mediate the same type of transformations as monooxygenases i.e. the incorporation of oxygen atom into the substrate but without consumption of cofactor. The necessary reducing equivalents are derived from hydrogen of hydrogen peroxide. More over peroxidases are generally extracellular enzymes and are considerably more robust than intracellular monooxygenases. One of the most common example belonging to this group is chloroperoxidase (CPO), produced from filamentous fungus *Caldariomyces fumago* a heameprotein which catalyses the epoxidation of unfunctionalised *cis* alkene in presence of hydrogen peroxide to produce epoxides of variable yields.



The epoxidation of alkenes catalysed by chloroperoxidase resembles closely to that of monooxygenases, except for the fact that the chloroperoxidase utilises molecular oxygen and a reducing agent such as NADH. Since chloroperoxidase is commercially available and has been cloned and over expressed it appears to be useful as “free monooxygenase” for synthetic applications. Certain epoxides with well defined absolute configuration may be obtained from halohydrins produced via chloroperoxidase catalysed addition of HOX to carbon carbon double bond.

Chloroperoxidase also catalyses the enantioselective asymmetric oxidation of sulphides using either hydrogen peroxide or chiral hydroperoxides as oxidation agent. In the latter case, enzyme is highly selective for the (R)-enantiomer of chiral hydroperoxides generating (R)-alcohols and unreacted (S)-hydroperoxides. In the oxidation of phenyl methyl sulphide using racemic 1-phenyl ethyl hydrogen peroxide as oxidant, the sulphide is selectively oxidised to (R)-sulphoxide with the concurrent formation of (S)-1-phenyl ethyl hydroperoxide and (R)-1-phenyl ethanol.

and inorganic salts as sources of oxygen but are now increasingly formulated with ammonium nitrate as the oxygen source. Composite propellants commonly use ammonium perchlorate to supply the oxygen required. The most common gaseous products of the oxidation-reduction reactions are hydrogen, water, carbon monoxide, carbon dioxide, and nitrogen.

Table. 6.1. Characteristics of burning and detonation.

<i>Characteristics</i>	<i>Burning</i> <i>Fuel</i>	<i>Propellant</i>	<i>Explosive</i> <i>detonation</i>
Typical material	coal-air	propellants	explosives
Linear reaction rate, m/s	10^{-6}	10^{-2}	$2-9 \times 10^{-3}$
Type of reactions	oxidation-reduction	oxidation-reduction	oxidation-reduction
Time for reaction completion, s	10^{-1}	10^{-3}	10^{-6}
Factor-controlling reaction rate	heat transfer	heat transfer	shock transfer
Energy output, J/g ^a	10^4	10^3	10^3
Power output, W/cm ²	10	10^3	10^{9b}
Most common initiation mode	heat	hot particles and gases	high temperature-high pressure shock waves
Pressure developed, MPa ^c	0.07-0.7	$0.7-7 \times 10^2$	$7 \times 10^3 - 7 \times 10^4$
Uses	source of heat and electricity	controlled gas pressure, guns, and rockets	brisance, blast, munitions, civil engineering

^a To convert J to cal, divide by 4.184.

^b This may be compared with the total United States electric-generating capacity of about 30×10^6 kW.

^c To convert MPa to psi, multiply by 145.

Explosive detonation

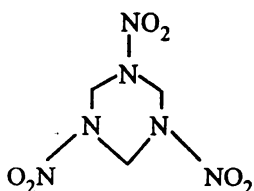
Detonation proceed as a result of a reaction front moving in a direction normal to the surface of the explosive. However, detonation is a hydrodynamic phenomenon that differs in a fundamental sense from burning. Upon initiation, burning first occurs at an increasing rate for period of time up to several micro-seconds. A high pressure shock wave

Manufacture

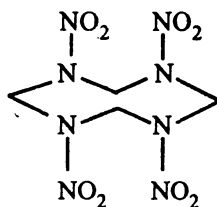
The batch nitration process have included the pot process, the centrifugal process, the Thompson displacement process, and the Mechanical Dipper process. In the batch process, the raw materials proceed by gravity through the processing operations. The nitration of cellulose occurs very rapidly at first and the nitrocellulose is separated from spent nitrating acid. Semi-continuous nitration processes have been developed for military and industrial grades. Semi-continuous nitration uses a multiple-cascade system and a continuous wringing operation. The controlling factors in the nitration process are the rates of diffusion of the acid into the fibres, the composition of the mixed acid, and the temperature.

Nitramines

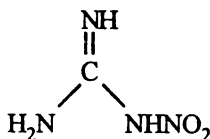
The four most important nitramines are: cyclotrimethylenetrinitramine (RDX); cyclotetramethylenetetranitramine (HMX); nitroguanidine (NQ); and 2,4,6-trinitrophenylmethylnitramine (tetryl). Tetryl has been increasingly replaced by RDX; both RDX and HMX are used as high energy explosives and may also be incorporated in high performance rocket propellants. Nitroguanidine is employed almost exclusively in gun propellants.



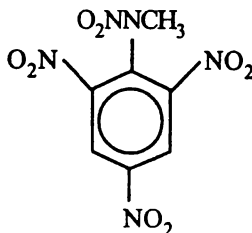
RDX



HMX



nitroguanidine



tetryl

Table 6.2. Typical components of nitrocellulose propellants and their function.

<i>Component</i>	<i>Application</i>
Nitrocellulose	energetic polymeric binder
Nitroglycerine, metriol trinitrate, diethylene glycol dinitrate,	plasticisers
Triethylene glycol dinitrate, dinitrotoluene	energetic
Dimethyl, diethyl or dibutyl phthalates, triacetin	plasticisers fuels
Diphenylamine, diethyl centralite, 2-nitrodiphenylamine	stabilisers
Organic and inorganic salts of lead; e.g., lead stannate, lead stearate, lead salicylate	ballistic modifiers
Carbon black	opacifiers
Lead stearate, graphite, wax	lubricants
Potassium sulphate, potassium nitrate, cryolite (potassium aluminium fluoride)	flash reducers
Ammonium perchlorate, ammonium nitrate	oxidisers inorganic
RDX, HMX, nitroguanidine and other nitramines	organic
aluminium	metallic fuels cross-linking catalysts
Lead carbonate tin	defouling agents

Polymer-based rocket propellants, referred to as composite propellants, contain a cross-linking polymer which acts as a viscoelastic matrix for holding a crystalline inorganic oxidiser such as ammonium perchlorate and for providing mechanical strength. Many other substances may be added including metallic fuels, plasticisers, extenders, and catalysts. Polymer-based composite propellants are too erosive to be used in guns because of the residues formed after repeated firings. Typical components of composite propellants are listed in Table 6.3.

Table 6.3. Typical components of composite rocket propellants.

<i>Typical components</i>	<i>Characteristics</i>
<i>Binders</i>	
Polysulphides	reactive group, mercaptyl ($-\text{SH}$), is cured by oxidation reactions; low solids loading capacity and relatively low performance; now mostly replaced by other binders
Polyurethanes polyethers	reactive group, hydroxyl ($-\text{OH}$), is cured with isocyanates; intermediate solids loading capacity and performance

(Contd...)