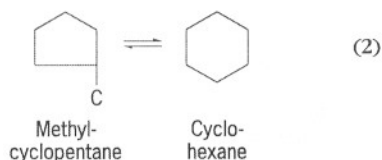


trichloride or used in the form of a liquid complex with hydrocarbon. A second type of catalyst for vapor-phase isomerization (300–850°F or 150–450°C) is a noble metal, usually platinum, supported on a carrier. This may be alumina with halide added to provide an acidic surface. All the processes are selective (95–98% to isobutane). Approximately 60% of the *n*-butane feed is converted per pass to isobutane in the liquid-phase process.

Isopentane, a high-octane component used in aviation gasoline, is made commercially by isomerization of *n*-pentane. Petroleum naphthas containing five- and six-carbon hydrocarbons also are isomerized commercially for improvement in motor-fuel octane numbers. Noble-metal catalyst is normally used with higher-molecular-weight feeds. Isomerization of paraffins above six carbon atoms is of less importance, since octane improvement is limited by predominance of monomethyl branching at equilibrium. Skeletal isomerization is an important secondary reaction in catalytic cracking and catalytic reforming. Aromatics and olefins undergo skeletal isomerization as do paraffins.

Single-carbon bond shift. This process, in the case of naphthenes, is illustrated by reaction (2). Cyclohexane and methylcyclohexane have been produced



commercially by liquid-phase isomerization of the five-carbon ring isomers over aluminum chloride-hydrocarbon-complex catalyst promoted by hydrogen chloride. Conversion per pass is high, selectivity excellent, and reaction conditions mild (190°F or 88°C). Cyclohexane is a raw material for making nylon, and it may be dehydrogenated to benzene. Methylcyclohexane has been used to make synthetic nitration-grade toluene.

Shift of a double-bond. This process is usefully applied when a specific olefin is needed for chemical synthesis, as in reaction (3). Double-bond shift



occurs selectively over acidic catalysts at temperatures below 450°F (230°C). However, the proportion undergoing skeletal isomerization increases as temperature is increased until, at temperatures in the range of 600–950°F (300–510°C), equilibrium is approached at fairly high space velocities. Equilibrium favors movement of double bonds to the more stable internal positions (85.6% 2-butene at 400°F or 200°C), and octane improvement accompanies this shift; however, the increase of octane number normally is insufficient to justify the cost of processing thermally cracked gasolines solely for this purpose. This type of isomerization occurs as a secondary reaction in the catalytic cracking and catalytic polymerization processes, in part accounting for the high oc-

tane numbers of the gasolines. See AROMATIZATION; CRACKING; MOLECULAR ISOMERISM; PETROLEUM PROCESSING AND REFINING.

George E. Liedholm

Isometric process

A constant-volume thermodynamic process in which the system is confined by mechanically rigid boundaries. No direct mechanical work can be done on the surroundings by a system with rigid boundaries; therefore the heat transferred into or out of the system equals the change of internal energy stored in the system. This change in the internal energy, in turn, is a function of the specific heat and the temperature change in the system as in Eq. (1), where Q_V

$$Q_V = U_2 - U_1 = \int_1^2 C_V dT \quad (1)$$

is the heat transferred at constant volume, U is the internal energy, C_V is the heat capacity at constant volume, and T is the absolute temperature. If the process occurs reversibly (the system going through a continuous sequence of equilibrium states), Eq. (2)

$$Q_V = \int_1^2 T dS \quad (2)$$

holds, where S is the entropy. There is an increase in both the temperature and the pressure of a constant volume of gas as heat is transferred into the system. For a comparison of the isometric process with other processes involving a gas see POLYTROPIC PROCESS

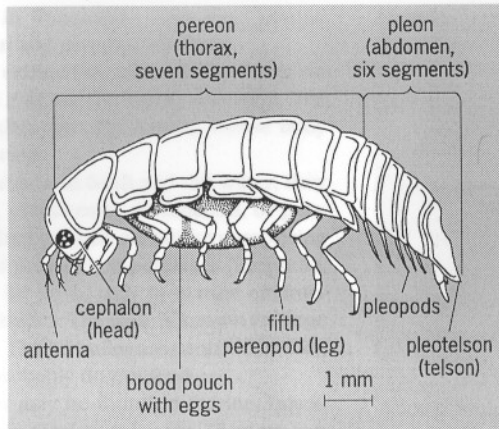
Philip E. Bloomfield

Isopoda

An order of invertebrate crustaceans related to crabs, shrimps, and lobsters, all members of the class Malacostraca. The closest relatives of Isopoda are the amphipods, mysids (opposum shrimps), cumaceans, and tanaids, all of which are placed in the super-order Peracarida. Isopods are generally small but very common, highly diversified, and occurring in marine, freshwater, and terrestrial habitats. Sow bugs, pill bugs, and woodlice, as well as their marine relatives (such as gribbles and sea slaters), belong to this group. See CRUSTACEA; MALACOSTRACA; PERACARIDA.

Morphology. Isopods are characterized by the lack of a carapace (an outer case or covering made of chitin), having the first thoracic segment fused with the head, one pair of maxillipeds (one of the four sets of paired mouthparts used for feeding), and usually seven pairs of similar legs, although the first leg may be clawlike. Adults of the suborder Gnathiidea possess five pairs of legs.

As in most crustaceans, the body has three parts: the head (cephalon), thorax (pereon), and abdomen (pleon) [see **illustration**]. The cephalon bears sessile eyes and two pairs of antennae, the first of which is chemosensory and the second tactile in function. Each of the seven segments of the pereon



Limnoria (Flabellifera), female. (After R. J. Menzies, *The comparative biology of the wood-boring isopod crustacean Limnoria*, Museum of Comparative Zoology, Harvard Coll. Bull., 112(5):363-388, 1954)

(pereonites) normally bears a pair of legs called pereopods. These are used for locomotion and grabbing prey. The abdomen typically consists of five segments or pleonites (which may be fused in some) plus a sixth segment called the pleotelson. Uropods are the paired appendages at the base of the pleotelson; these are used in orientation and swimming. Each of the pleonites has a ventral pair of foliaceous appendages (leaflike pleopods) which are used for swimming and respiration.

Ecology. At present there are more than 10,400 described species of isopods. Of those, about 4200 species are terrestrial, and these include the familiar sow bugs, pill bugs, roly-polys, and woodlice. They may be found in any habitat on land, including forests, caves, deserts, city sidewalks, and greenhouses.

Terrestrial isopods feed on algae, moss, bark, and decaying plant and animal matter. Like insects, they play a role in the breakdown and recycling of organic nutrients. Cellulose digestion results from the presence of bacteria in the digestive system.

In the continental United States and Canada, there are about 120 known species of terrestrial isopods. The most common are widely distributed and have probably been introduced from Europe. A majority of the most abundant species in North America are concentrated in the northeast and northwest, possibly a result of the transport of their ancestors into harbors by human immigrants.

Marine isopods, numbering more than 5600 species, are found at all latitudes and in all marine habitats, from the intertidal zone to the deep sea, including coral reefs, sponges, algae, and seagrass beds. They range in size from less than a millimeter (<0.04 in.) [one of the parasitic forms] to 1.5 mm (0.06 in.) [*Microcharon*, found living between sand grains] to 44 cm (17.3 in.) [*Bathynomus* in the depths of the Caribbean Sea]. A few, such as *Idothea*, are cosmopolitan (having worldwide distribution), perhaps being distributed by floating on rafts of seaweed. Others travel in ballast water in

ocean-going ships from place to place.

Because they have limited swimming ability and move chiefly by crawling on the bottom, most isopods have relatively small ranges. They recycle nutrients by eating detritus, both plant and animal material, and become part of the food chain in the sea as they are eaten by larger animals, particularly fish. Marine isopods may be omnivores, herbivores, or predators; some specialize as parasites, living off fluids and tissues of their hosts, mainly fish and other crustaceans. They fulfill many of the same ecological niches as insects.

The isopod species found in freshwater total about 600. Their habitats include rivers, subterranean streams, caverns, wells, swamps, and hot springs. They tend to have very restricted habitats and thus are the most likely isopods to be designated as threatened or endangered species.

Reproductive biology. As is typical of the peracarids, isopods develop inside the female brood pouch (marsupium) located on the underside of the abdomen. When the young emerge, they typically lack the seventh pair of legs and are known as manca but otherwise look like adults (except in Gnathiidea). Some evidence of parental care has been recorded in the family Sphaeromatidae (suborder Flabellifera); and in *Iais* (suborder Asellota) adults are known to carry the manca about by clasping it to their ventral abdomen. Mate guarding has also been observed. Examples of sequential hermaphroditism or sex change have been found in several groups, both male-to-female and female-to-male. However, sexes are usually separate and can be virtually identical or widely divergent in morphology, depending on the suborder or family.

Evolution. Isopods date from the Paleozoic Era, when malacostracans as a group underwent a rapid evolution. The earliest fossil records of isopods contain members of the present-day Phreatoicoidea, dating 325 million years ago, representing a very early offshoot from the original common ancestor. These animals, currently found only in freshwater habitats, are only slightly changed from their fossil ancestors and may be considered as living fossils (living species belonging to an ancient stock otherwise known only as fossils.) Other isopod groups probably evolved as benthic (bottom) dwellers in shallow marine environments such as estuaries and embayments before radiating into the deep sea, and they also conquered land as the only truly terrestrial crustaceans (suborder Oniscidea). *Cyclospira* from the Jurassic, discovered in England, is related to members of the contemporary family Sphaeromatidae.

Classification. The classification system currently in wide use recognizes 10 suborders, listed below.

Anthuridea are generally elongate and cylindrical, living in soft bottoms of estuaries and oceans, especially in tropical reef environments.

Asellota are very diverse, are generally herbivores, and live in freshwater as well as marine habitats. They are particularly diverse in the deep sea. One pair of pleopods forms a cover over the rest of the pleopods.

Calabozeidea have been found thus far only in

freshwater wells in Venezuela. They have unique body segmentation and pleopod structure.

Epicaridea are exclusively external parasites on other crustaceans and may be highly modified. The male is much smaller than the female, whose body may be very distorted.

Flabellifera inhabit both fresh and salt water; they can be free-living, predaceous, commensal, or parasitic. A common characteristic is a tail fan comprising the pleotelson and posterior appendages (uropods).

Gnathiidea can be found only in marine environments but at all latitudes. The male is known for large frontal mandibles. The juveniles are parasitic on fish, while the adults probably do not feed.

Microcerberidea may be found in marine, brackish, or fresh water in sand or sediment. They are less than 2 mm (0.08 in.) in length.

Oniscidea, the sow bugs or pill bugs, have successfully conquered almost all terrestrial habitats, as their pleopods are adapted for breathing air.

Phreatoicidea, relict (being a persistent, isolated remnant of a once-abundant species) crustaceans, are found thus far only in Australia, Tasmania, and South Africa. They are laterally compressed with long antennae and long uropods.

Valvifera have uropods which are flexed beneath the abdomen and cover the pleopods. Many live on seaweed or seagrass, from the tropics to the polar regions.

Several authors (A. Brandt and G. C. B. Poore) have suggested that the Flabellifera is an artificial grouping, so further reorganization of this system is certain. These authors have also erected two new suborders, Tainisopodidea, including members of the family Tainisopodidae, found only in ground waters in western Australia, and Phoratopidea, comprising a single species found only in Australia. Marilyn Schotte

Bibliography. A. Brandt and G. C. B. Poore, Higher classification of the flabelliferan and related Isopoda based on reappraisal of relationships, *Invert. Systemat.*, 17(6):893-923, 2003; G. Brusca and R. C. Brusca, *Invertebrates*, Sinauer Associates, Sunderland, 1990; B. Kensley and M. Schotte, *Guide to the Marine Isopod Crustaceans of the Caribbean*, Smithsonian Institution Press, Washington, DC, 1989; B. Kensley, M. Schotte, and S. Schilling, *World List of Marine, Freshwater and Terrestrial Crustacea Isopoda*, Smithsonian Institution, Washington, DC, 1996; M. R. Warburg, *Evolutionary Biology of Land Isopods*, Springer-Verlag, Berlin, 1993.

Isoprostanes

A class of natural products discovered relatively recently. The isoprostanes (iPs) are isomeric with another class of natural products, the prostaglandins. The prostaglandins are the result of enzymatic oxygenation of polyunsaturated fatty acids (PUFAs), in particular arachidonic acid (AA). In contrast, the iPs are formed in vivo by a nonenzymatic, free-radical oxygenation of arachidonic acid. This important distinction in the mode of formation of the iPs is

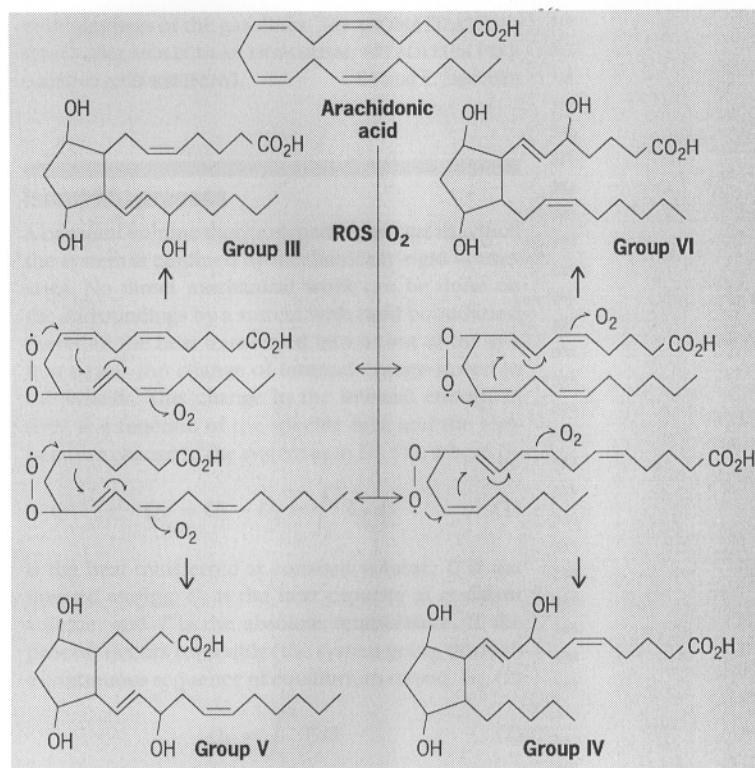


Fig. 1. Endoperoxide mechanism for the formation of isoprostanes.

sponsible for a more complex mixture of iPs being generated in vivo. For example, whereas the endoperoxide prostaglandin G_2 (PGG_2) is formed by the cyclooxygenase enzymes (COX1 and COX2), four classes of iPs are formed as result of the free-radical oxygenation of arachidonic acid each class containing 16 iPs for a total of 64 individual iP molecules (Fig. 1). The discovery of iPs is important for two reasons: (1) group III iPs are incidental ligands for the prostaglandin receptors, hence they possess biological activity. (2) iPs are the product of oxidative stress. Their measurements have been shown to be a predictor of the onset and severity of inflammatory diseases such as Alzheimer's disease and atherosclerosis. See ALZHEIMER'S DISEASE; CIRCULATION DISORDERS; EICOSANOIDS; FREE RADICAL.

Mechanism for formation. Two mechanisms for the formation of iPs have been proposed based on in-depth regiochemical and stereochemical analysis of the peroxidation process. These are the endoperoxide mechanism (Fig. 1) and the dioxetane mechanism. Recently, evidence has been reported showing that the dioxetane mechanism may not be operative.

A more detailed mechanistic view for the formation of group VI iPs by the endoperoxide mechanism is presented in Fig. 2. The four iPs shown in the box have been prepared by total synthesis and used in discovery and identification of the same products in human urine (Fig. 4).

Nomenclature. A comprehensive nomenclature for iPs has been introduced utilizing the symbols in the prostaglandin nomenclature. The new classification