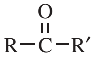
# KETONES

## 1. Introduction

Ketones are a class of organic compounds that contain one or more carbonyl groups bound to two aliphatic, aromatic, or alicyclic substituents, and are represented by the general formula



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R'$$

Ketones are named by selecting as the parent compound the longest carbon chain that contains the carbonyl group and replacing the terminal "-e" of the parent compound by "-one". The parent chain is numbered in the direction that gives the carbonyl group the lowest number. $CH_3COCH_2CH_3$ is named 2-butanone. In the naming of complex carbonyl structures containing more than one functional group, the carbonyl group takes precedence over alkene, hydroxyl, and most other groups. An older system of naming ketones simply lists the names of the R and R′ groups attached to the carbonyl group, followed by the word "ketone". By using this nomenclature, 2-butanone is named methyl ethyl ketone.

Ketones are an important class of industrial chemicals that have found widespread use as solvents and chemical intermediates. Acetone is the simplest and most important ketone and finds ubiquitous use as a solvent. Higher members of the aliphatic methyl ketone series (eg, methyl ethyl ketone, methyl isobutyl ketone, methyl amyl ketone) are also industrially significant solvents. Cyclohexanone is the most important cyclic ketone and is primarily used to manufacture a precursor for nylon-6. Other ketones find application in fields as diverse as fragrance formulation and metals extraction. Although the industrially important ketones are reviewed herein, the laboratory preparation of ketones is covered elsewhere (1). Table 1 lists some common ketones with their common names, systematic names, and synonyms for easy reference.

The lower molecular weight aliphatic ketones and cycloaliphatic ketones are stable, colorless liquids and generally have a pleasant, slightly aromatic odor. They are relatively volatile, with boiling points slightly above those of corresponding alkanes. Unsymmetrical ketones are lower melting and higher boiling than corresponding symmetrical ketones. The members of the series up to $C_5$ are fairly soluble in water and are excellent solvents for nitrocellulose, vinyl resin lacquers, cellulose ethers and esters, and various natural and synthetic gums and resins.

In contrast, aromatic ketones are high boiling, colorless liquids that generally have a fragrant odor and are almost insoluble in water. They are useful as intermediates in chemical manufacture. Functionalized and cyclic ketones are also good solvents. Ring size and the type and location of functional groups affect odor, color, and reactivity of these ketones.

The physical properties of the common ketones listed in Table 1 are given in Tables 2 and 3. Table 2 lists the important pure compound properties. In addition, some ketone–water binary mixture properties are also of practical interest; these include mutual solubilities, azeotropes, and Henry's law constants of ketones in dilute aqueous solutions. These properties are listed in Table 3.

Ketones are commonly separated by fractional distillation. The vapor–liquid equilibria and vapor pressure data are readily available for common ketones (15,16). A number of other temperature-dependent physical properties for acetone, methyl ethyl ketone, methyl isobutyl ketone, and diethyl ketone have been published (17). Ketones, like aldehydes, tend to form azeotropes with water and other substances. The ketone–water azeotropes for some common ketones are included in Table 3. Most ketones are not completely soluble in water; such a ketone normally forms a heterogeneous minimum-boiling azeotrope with water, as indicated in Table 3.

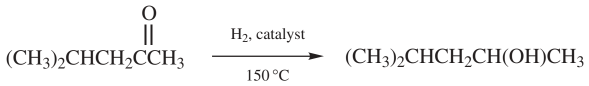
Another practically important ketone–water mixture property is the Henry's law constant (HLC), which measures the volatility of a chemical in a dilute aqueous solution instead of by itself. It is of great interest to environmental issues involving contaminated water. This parameter provides an indication of how much of the pollutant may be released to the atmosphere from a polluted water source and how much of it can be removed from the water by air or steam stripping. However, the HLC is difficult to measure accurately, and there are few directly measured data in the literature. Most of the available data are either calculated from other measured properties such as vapor pressure and water solubility or estimated based on the molecular structure; these data for a specific compound can differ by several orders of magnitude. Fortunately, many practical applications need HLCs only to order-of-magnitude accuracy. The EPA is compiling a databank of HLCs for organic chemicals, and the CMA is reviewing this tentative databank (13). The HLCs for common ketones from this tentative databank are given in Table 3. In addition, Table 3 provides another set of HLCs calculated from other measured properties along with a set of estimation methods (14) for comparison.

## 2. Chemical Properties

The constituent carbonyl group makes many of the reactions and methods of preparation for ketones similar to those of aldehydes. Ketones, however, generally undergo 1,2-addition reactions across the carbonyl group less readily than aldehydes because of steric hindrance around the carbonyl group. Similarly, the relative reactivity among ketones is influenced by the polarity and electrophilic nature of the substituents in the vicinity of the carbonyl group (eg, hydrogens alpha to the carbonyl group). The chemical properties of diketones, and cyclic and unsaturated ketones such as 2,4-pentanedione, cyclohexanone, and mesityl oxide, respectively, are enhanced, thereby increasing their utility as chemical intermediates.

### 2.1. Reduction.

Most ketones are readily reduced to the corresponding secondary alcohol by a variety of hydrogenation processes. The most commonly used catalysts are palladium, platinum, and nickel. For example, 4-methyl-2-pentanol (methyl isobutyl carbinol or methyl amyl alcohol) is commercially produced by the catalytic reduction of 4-methyl-2-pentanone (methyl isobutyl ketone) over nickel.



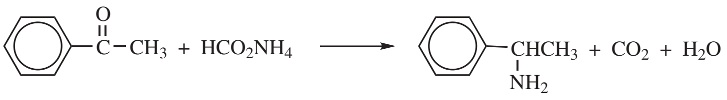
$$(\mathrm{CH_3})_2\mathrm{CHCH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3} \xrightarrow[150\,^{\circ}\mathrm{C}]{\mathrm{H_2,\ catalyst}} (\mathrm{CH_3})_2\mathrm{CHCH_2CH(OH)CH_3}$$

**2.2. Oxidation.** Ketones are oxidized with powerful oxidizing agents such as chromic or nitric acid. During oxidation, carbon–carbon bond cleavage occurs to produce carboxylic acids. Ketone oxidation with hydrogen peroxide, or prolonged exposure to air and heat, can produce peroxides. Concentrated solutions of ketone peroxides (>30%) may explode, but dilute solutions are useful in curing unsaturated polyester resin mixtures (see PEROXIDES AND PEROXIDE COMPOUNDS).

**2.3. Condensation.** *Base Catalyzed.* Depending on the nature of the hydrocarbon groups attached to the carbonyl, ketones can either undergo self-condensation, or condense with other activated reagents, in the presence of base. Named reactions that describe these conditions include the Darzens–Claisen condensation, the Claisen–Schmidt condensation, and the Michael reaction. The aldol reaction belongs in this category as well.

*Acid Catalyzed.* Although ketonic carbonyl groups are less reactive than aldehydic carbonyls in the presence of basic catalysts, this is not the case with acid catalysts. Thus acetone undergoes aldol addition in the presence of sulfuric acid to give mesityl oxide, which then condenses with a third molecule of acetone to give a mixture of phorone (2,6-dimethyl-2,6-heptadien-4-one) and mesitylene (1,3,5-trimethylbenzene). Ketones also condense with activated aromatic products in the presence of sulfuric acid to give coupled aromatic products. For example, acetone and phenol condense to bisphenol A (4,4′-isopropylidenediphenol), which is used in the manufacture of epoxy resins and polycarbonates.

**2.4. Preparation of Amines.** Amines can be prepared by heating aliphatic, aromatic, or cyclic ketones with ammonium formate, formamide, or an N-substituted ammonium formate at 165–190°C (Leuckart reaction). For example, α-methylbenzylamine is prepared by the reaction of acetophenone with ammonium formate.



**2.5. Thermal Stability.** The saturated $C_4$–$C_{12}$ ketones are thermally stable up to pyrolysis temperatures (500–700°C). At these high temperatures, decomposition can be controlled to produce useful ketene derivatives. Ketene itself is produced commercially by pyrolysis of acetone at temperatures just below 550°C (see KETENES, KETENE DIMERS, AND RELATED SUBSTANCES).

Some unsaturated ketones derived from acetone can undergo base- or acid-catalyzed exothermic thermal decomposition at temperatures under 200°C. Experiments conducted under adiabatic conditions indicate that mesityl oxide decomposes at 96°C in the presence of 5 wt% aqueous sodium hydroxide (20%), and that phorone undergoes decomposition at 180°C in the presence of 1000 ppm iron. The decomposition products from these reactions are endothermic hydrolysis and cleavage back to acetone, and exothermic aldol reactions to heavy residues.

## 3. Economic Aspects

Ketones of industrial importance are commercially available from chemical manufacturers. For convenient reference, Table 4 lists market prices and major producers, along with their current capacities for industrial ketones. The prices are intended to provide a relative cost comparison among ketones. Since the most important ketones, including acetone, methyl ethyl ketone, methyl isobutyl ketone, and cyclohexanone are manufactured by a lot of producers and are discussed in detail in separate articles, Table 4 lists only the largest few producers for these ketones (U.S. producers only for acetone and cyclohexanone).

## 4. Health and Safety Factors

Ketones do not exhibit a known high degree of chronic toxicity. Low molecular weight ($C_3$–$C_{12}$) saturated aliphatic ketones, which represent the bulk of industrially important ketones, may be classified among the solvents of comparatively low toxicity hazard. The 8-h threshold limit value is generally $>100$ ppm, although the odor threshold is in the range 5–25 ppm (23). High vapor concentrations of these volatile ketones induce anesthesia. However, the vapors are so irritating to the eyes and mucous membranes of the respiratory system that the atmosphere generally becomes intolerable before toxic concentrations are achieved. The use of ketones in confined areas, such as during tank cleaning, is one example in which adequate ventilation is required. Many ketones are also powerful drying and degreasing agents, and prolonged skin contact can cause dermatitis. The toxicity of unsaturated ketones and diketones is significantly greater. The 8-h threshold limit value for these materials is $\leq 50$ ppm. Table 5 shows the toxicological properties and exposure limits of some common ketones. A detailed review of the physiological effects of exposure to methyl ethyl ketone and methyl isobutyl ketone has been documented (25).

Ketones are flammable substances. The $C_3$–$C_{12}$ aliphatic ketones are all highly flammable liquids with flash points varying from −18°C for acetone to 85°C for isobutyl heptyl ketone. Ketones float on water, and become only partially soluble in water with increasing molecular weight. Thus, ketones typically require copious quantities of water to extinguish pool fires. Saturated ketones are in general stable at ambient conditions, and do not undergo hazardous polymerization in normal environment. Most ketones are incompatible with strong oxidizing and reducing agents; some ketones are also incompatible with bases and/or acids. Table 6 lists the flammability parameters and stability information of some common ketones.

## 5. Environmental Aspects

Most industrially important ketones are volatile organic compounds (VOCs), which are subject to air pollution control regulations. The purpose of these regulations is to limit the atmospheric release of materials that could be either toxic or precursors of ozone and other species associated with photochemical smog. Legislation has become progressively more stringent as the long-term effects of atmospheric pollution have become evident. In the United States, most states have developed their own programs to govern the release of toxic air pollutants. Pertinent federal regulations include the Clean Air Act (CAA) with major amendments in 1990 and the Superfund Amendments and Reauthorization Act (SARA), Title III Section 313 (see AIR POLLUTION). The 1990 CAA Amendments list ~200 hazardous air pollutants (HAPs) that the EPA must regulate to enforce maximum achievable control technology (MACT) to standards, which were to be set by the year 2000. The SARA 313 statute provides a mechanism by which the community can be informed of the existence, quantities, and releases of toxic chemicals, and requires that anyone releasing specific toxic chemicals above a threshold level to annually submit a toxic chemical release form to the EPA. The impact of these regulations on ketones is to require users and producers of VOC ketones to limit release by either reformulating to new solvent systems, installing environmental control systems that recover and recycle solvents, or reducing emissions with carbon adsorption beds or incineration equipment.

In addition to the foregoing regulations on air pollutants, some ketones are governed by other federal laws for environmental protection. In the United States the key regulations include the Clean Water Act (CWA) to control toxic water pollutants, the Resource Conservation and Recovery Act (RCRA) to manage hazardous wastes from generation to disposal (from cradle to grave), and the Toxic Substance Control Act (TSCA) to track industrial chemicals produced or imported. For convenient reference, Table 7 lists the status of industrial ketones under these U.S. environmental regulations.

## 6. Aliphatic Ketones

The three most important aliphatic ketones are acetone, methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK), which are discussed in detail in separate articles (see ACETONE, METHYL ISOBUTYL KETONE). Other important aliphatic ketones are discussed in this section.

### 6.1. Diacetone Alcohol.

Diacetone alcohol (DAA) [123-42-2] (4-hydroxy-4-methyl-2-pentanone) is a colorless, mild-smelling liquid that is completely miscible with water and most organic solvents. It is the simplest aldol condensation product of acetone. Because of its keto-alcohol functionalities, it has special utility in the coatings industry, where it is used to dissolve cellulose acetate to give solutions with high tolerance for water (32).

*Manufacture.* DAA is manufactured by the low temperature liquid-phase self-condensation of acetone in the presence of a solid base catalyst. The reaction is exothermic (−14.6 kJ/mol = −3.49 kcal/mol) (33), and is equilibrium limited (34). The unfavorable effect of increasing temperature on the equilibrium constant has been documented (33); the equilibrium concentration of DAA, which is 23.1 wt% at 0°C, declines to 9.1 wt% at 30°C. Although low temperatures favor DAA formation, kinetic considerations require that commercial operation be conducted at 10–20°C. Either single- or multistage catalyst beds can be used: single-stage conversion requires lower inlet temperatures, multistage conversion can cascade to progressively lower inlet temperatures (35). Residence times of 20–60 min are typically required.

Suitable catalysts include the hydroxides of sodium (36), potassium (37,38), calcium (39–43), and barium (44–48). Many of these catalysts are susceptible to alkali dissolution by both acetone and DAA and yield a crude product that contains acetone, DAA, and traces of catalyst. To stabilize DAA; the solution is first neutralized with phosphoric acid (49) or dibasic acid (50). Recycled acetone can then be stripped overhead under vacuum conditions, and DAA further purified by vacuum topping and tailing. Commercial catalysts generally have a life of ~1 yr and can be reactivated by washing with hot water and acetone (51). It is reported (52) that addition to a calcium hydroxide catalyst of 0.2–2 wt% methanol, ethanol, or 2-propanol helps prevent catalyst aging. Research has reported the use of more mechanically stable anion-exchange resins as catalysts (53–55). The addition of trace methanol to the acetone feed is beneficial for the reaction over anion-exchange resins (56).

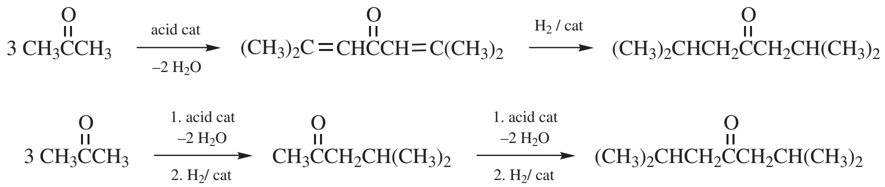
Early patents indicated that because water inhibits the aldol condensation mechanism, it was necessary to dry recycled acetone to <1% water (57–60). More recent reports demonstrate DAA production from waste acetone containing 10–50% water (61), and enhanced DAA production over anion-exchange resins using acetone feeds that contain 3–10% water (62,63).

Industrially, a selectivity to DAA of between 90 and 95% can be achieved (64). The principal by products are mesityl oxide and acetone trimers. sym-Triacetone dialcohol [3682-91-5] can form by condensation of acetone with DAA (33). Dehydration of sym-triacetone dialcohol can yield semiphorone [5857-71-6] (6-hydroxy-2,6-dimethyl-2-hepten-4-one), which may in turn ring close to form 2,2,6,6-tetramethyl-γ-pyrone [1197-66-6], or ultimately dehydrate to phorone [504-20-1] (2,6-dimethyl-2,5-heptadien-4-one) (65). Similarly, an unsymmetrical acetone trimer can also be formed that dehydrates to 2,4-dimethyl-2,4-heptadiene-6-one. These impurities complicate the high purity recovery of DAA and are thought to be responsible for a yellow discoloration of DAA. The addition of dibasic acid (66) or nitrogen-containing carboxylic or phosphonic acids (67) has been patented as refined product stabilizing agents.

*Uses.* Diacetone alcohol is a widely used solvent in the coatings industry, where it finds application in hot lacquers that require high boiling components, and in brushing lacquers where its mild odor, blush resistance, and flow-out properties are desired. Diacetone alcohol is also a solvent for nitrocellulose, cellulose acetate, and epoxy resins.

In addition to its use in the production of MIBK, DAA finds use as a specialty reaction intermediate. Hydrogenation of DAA at 100°C and 30 MPa (68) yields hexylene glycol [107-41-5] (2-methyl-2,4-pentanediol), which is widely used in castor oil-based hydraulic brake fluids and as a solvent. Reaction of p-phenetidine [156-43-4] with DAA synthesizes Monsanto's Santoquin (ethoxyquin) [91-53-2] (69), an antioxidant used in animal feeds and also as a rubber additive.

**6.2. Diisobutyl Ketone.** Diisobutyl ketone (DIBK) [108-83-8] (2,6-dimethyl-4-heptanone) is a colorless stable liquid with a peppermint odor. DIBK can be produced by the hydrogenation of phorone which, in turn, is produced by the acid-catalyzed aldol condensation of acetone. It is also a coproduct in the manufacture of MIBK via aldol condensation of acetone followed by hydrogenation because it is generated via aldol condensation of acetone and MIBK followed by hydrogenation:



$$3\,CH_3\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[-2\,H_2O]{\text{acid cat}} (CH_3)_2C{=}CH\overset{O}{\overset{\|}{C}}CH{=}C(CH_3)_2 \xrightarrow{H_2/\text{ cat}} (CH_3)_2CHCH_2\overset{O}{\overset{\|}{C}}CH_2CH(CH_3)_2$$

$$3\,CH_3\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[\text{2. }H_2/\text{ cat}]{\substack{\text{1. acid cat}\\ -2\,H_2O}} CH_3\overset{O}{\overset{\|}{C}}CH_2CH(CH_3)_2 \xrightarrow[\text{2. }H_2/\text{ cat}]{\substack{\text{1. acid cat}\\ -2\,H_2O}} (CH_3)_2CHCH_2\overset{O}{\overset{\|}{C}}CH_2CH(CH_3)_2$$

For the coproduction of MIBK and DIBK via aldol condensation, the ratio of these two products is a function of the reaction temperature and feed rate. However, the reaction temperature is normally used to compensate for the catalyst deactivation and the feed rate is usually determined by the desired overall production rate. Neither variable has much room for controlling the DIBK/MIBK ratio, which may not match the market demand. The capability to control this product ratio has recently been enhanced by a technology using a recycle of the reaction intermediates as another production mix control agent (70).

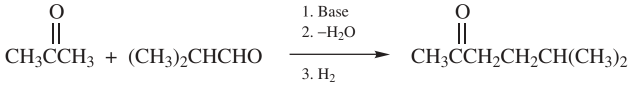
A commercial DIBK product typically contains ~15% of the isomer 4,6-dimethyl-2-heptanone [19549-80-5] (6), which is coproduced from the foregoing condensation reactions. Because its properties are similar to those of DIBK, this isomer is difficult to separate from DIBK, but for the same reason it can be used along with DIBK for most applications. DIBK is mainly used as a coating solvent. With more stringent regulations on VOCs, high volatility ketone solvents have been gradually replaced by low volatility ketones like DIBK. Therefore the market demand and price of DIBK have been increasing. Another major use of DIBK is in the production of diisobutyl carbinol [108-82-7] (2,6-dimethyl-4-heptanol) via catalytic hydrogenation. This alcohol is used in coatings formulations and peroxide manufacture.

**6.3. Methyl Isopropyl Ketone.** Methyl isopropyl ketone (MIPK) [563-80-4] (3-methyl-2-butanone) is a colorless liquid with a characteristic odor of lower ketones. It can be produced by hydrating isoprene over an acidic catalyst at 200–300°C (71,72) or by acid-catalyzed condensation of MEK and formaldehyde to 2-methyl-1-buten-3-one, followed by hydrogenation to the product (73). Other patented preparations are known (74–77). MIPK is used as an intermediate in the production of pharmaceuticals and fragrances (see PERFUMES), and as a solvent (78).

**6.4. Methyl Amyl Ketone.** Methyl amyl ketone (MAK) [110-43-0] (2-heptanone) is a colorless liquid with a faint fruity (banana) odor. It is found in the oil of cloves and cinnamon-bark oil, and is manufactured by the condensation of acetone and butyraldehyde (79). Other preparations are known (80–83). MAK is used as a high solids coating solvent (84) and in fragrances.

### 6.5. Methyl Isoamyl Ketone.

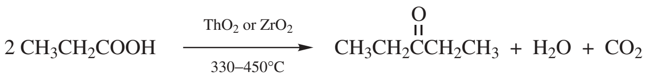
Methyl isoamyl ketone (MIAK) [110-12-3] (5-methyl-2-hexanone) is a colorless liquid with a mild odor. It is produced by the condensation of acetone and isobutyraldehyde (85) in three steps, which proceed via the keto-alcohol dehydration to 5-methyl-3-hexen-2-one, and hydrogenation to 5-methyl-2-hexanone. Isobutyraldehyde is commonly available as a by-product of propylene/oxo hydroformylation. MIAK is used as a solvent for cellulose esters, acrylics, and vinyl polymers.



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}CH_3 + (CH_3)_2CHCHO \xrightarrow[3.\ H_2]{1.\ Base\quad 2.\ -H_2O} CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH(CH_3)_2}$$

### 6.6. Diethyl Ketone.

Diethyl ketone (DEK) [96-22-0] (3-pentanone) is isomeric with methyl n-propyl ketone (2-pentanone), which has similar solvent and physical properties. DEK is produced by the decarboxylation of propionic acid over $MnO_2$–alumina (86), $ZrO_2$ (87), or $ZrO_2$ or $ThO_2$ on $TiO_2$ (88,89). It can also be produced by the hydrocarbonylation of ethylene (90–92). DEK is used as a solvent and a reaction intermediate.



$$\mathrm{2\ CH_3CH_2COOH \xrightarrow[330\text{–}450°C]{ThO_2\ or\ ZrO_2} CH_3CH_2\overset{\overset{O}{\|}}{C}CH_2CH_3 + H_2O + CO_2}$$

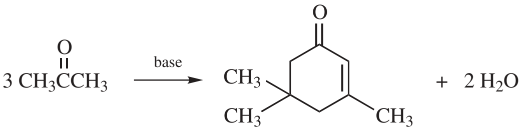
### 6.7. Isobutyl Heptyl Ketone.

Isobutyl heptyl ketone (IBHK) [123-18-2] (2,6,8-trimethyl-4-nonanone) is a by-product from the coproduction of MIBK and DIBK via aldol condensation of acetone followed by hydrogenation. It is generated by aldol condensation of two MIBK molecules or DIBK isomer (4,6-dimethyl-2-heptanone) and acetone followed by hydrogenation. IBHK has been largely converted via hydrogenation to 2,6,8-trimethyl-4-nonanol, a surfactant precursor. With the trend toward low volatility solvents, IBHK may find additional use in solvent applications.

## 7. Unsaturated Ketones.

### 7.1. Isophorone.

Isophorone [78-59-1] (3,5,5-trimethyl-2-cyclohexen-1-one) is a cyclic α,β-unsaturated ketone derived from the trimerization of acetone. It has a light yellow color and a disagreeable camphoraceous odor. It has a tendency to discolor and form residues on prolonged storage. Isophorone is completely miscible with organic solvents.



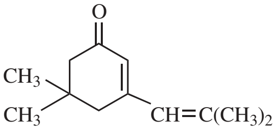
Isophorone usually contains 2–5% of the isomer β-isophorone [471-01-2] (3,5,5-trimethyl-3-cyclohexen-1-one). The term α-isophorone is sometimes used in referring to the α,β-unsaturated ketone, whereas β-isophorone connotes the unconjugated derivative. β-Isophorone is lower boiling than isophorone and can be converted to isophorone by distilling at reduced pressure in the presence of p-toluenesulfonic acid, phosphoric acid, or potassium hydrogen sulfate (93). Isophorone can be converted to β-isophorone by treatment with adipic acid (94) or iron(III) acetylacetoate (95). β-Isophorone can also be prepared from 4-bromoisophorone by reduction with chromous acetate (96). β-Isophorone can be used as an intermediate in the synthesis of carotenoids (97).

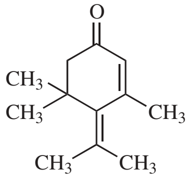
*Manufacture.* Isophorone is produced by aldol condensation of acetone under alkaline conditions. Severe reaction conditions are required to effect the condensation and partial dehydration of three molecules of acetone. Because isophorone can be further condensed with acetone under such conditions to heavier by-products, a low conversion is typically employed to achieve a desirable raw material efficiency. Both liquid- and vapor-phase continuous technologies are practiced (98–100).

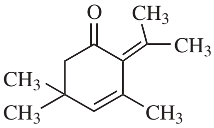
A liquid-phase isophorone process involves reactive distillation, as depicted by Figure 1 (68,101). A mixture of acetone, water, and potassium hydroxide (0.1%) is fed to a pressure column; which operates at head conditions of 205°C and 3.5 MPa (∼500 psi). Acetone condensation reactions occur on the upper trays, high boiling products move down the column, and unreacted acetone is distilled overhead in a water–acetone azeotrope, which is recycled to the column as reflux. In the lower section of the column, water and alkali promote hydrolysis of reaction by-products to produce both isophorone and recyclable acetone. Acetone conversion is typically in the range 6–10% and ∼70% yield of isophorone is obtained. Condensation–hydrolysis technology employing the same or other catalysts (101–106) and other liquid-phase production processes (107–113) have been reported.

In the vapor phase, acetone vapor is passed over a catalyst bed of calcium oxide (114), magnesium aluminate (115), zinc oxide–bismuth oxide (116), lithium or zinc-doped mixed magnesia–alumina (117), calcium on alumina (118), basic mixed-metaloxide catalysts (119–125), or zeolites (126). Temperatures ranging from 250 to 400°C and liquid hourly space velocity (LHSV) of 0.5–1.0 are employed.

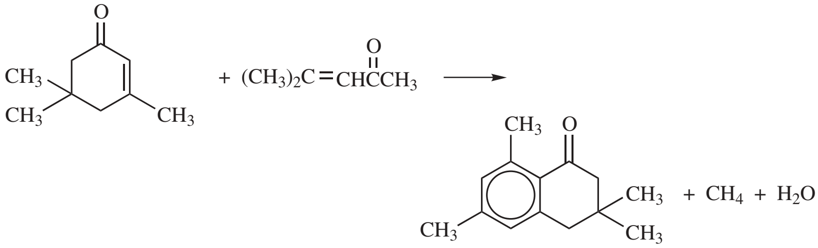
The liquid-phase processes are more energy efficient than the vapor-phase processes. However, they incur costly investment of high pressure equipment and also produce waste streams containing used catalyst (122). Both methods produce substantial quantities of by-products, which cause refining difficulties. The by-products consist primarily of mesitylene [108-67-8] (1,3,5-trimethylbenzene), phorone [504-20-1] (2,6-dimethyl-2,5-heptadien-4-one), and the following xylitone isomers (127):







Substantial amounts of 3,3,6,8-tetramethyl-1-tetralone [5409-55-2] are also formed, most notably in the vapor-phase process (128). This tetralone has been synthesized from isophorone and mesityl oxide, and it can thus be assumed to be a product of these two materials in the isophorone process (129,130).



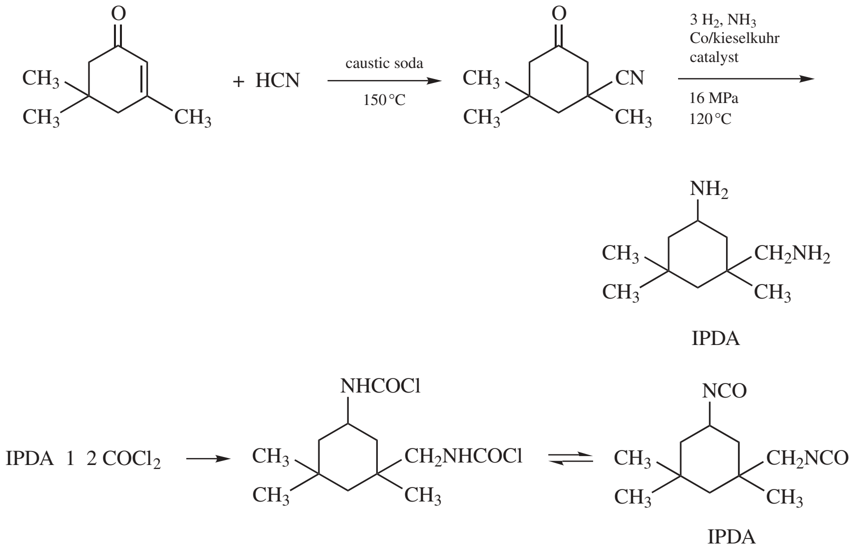
Some reversion of the overcondensate residues to acetone and isophorone is possible by hydrolysis with 2% sodium hydroxide solution at 175°C (131) and 0.9 MPa (102).

The crude isophorone refining operation can require as many as three or four distillation columns and is often conducted under vacuum to limit further by-product formation at high temperatures. Discoloration treatment during refining is often required to meet coatings industry requirements and to prolong storage life; various treatments using p-toluenesulfonic acid (105,132), oxalic acid (133), acidified fuller's earth (134), diazines (135), diisopropylamine (136), polyhydroxybenzene (137), aqueous caustic (138), and ion exchange (139,140) have been patented. Refined isophorone (99%) typically has a platinum–cobalt value of ~30–50 (APHA).

*Uses.* Isophorone has traditionally been used predominantly as a low volatility solvent. It exhibits powerful solvation power for a large number of natural and synthetic polymers, resins, fats, and oils. Of note is its use as a solvent for formulating highly concentrated vinyl chloride–acetate based coating systems for metal cans, nitrocellulose finishes, and as a leveling aid to prevent blistering and promote flow for uniform wetting of metal paints based on polyacrylates, alkyds, and epoxy and phenol–formaldehyde resins (141). In addition, it is used as a solvent for insecticide and herbicide concentrates, where it is employed to produce high emulsibility and good emulsion stability in aqueous dilution (68) (see Herbicides; Insect control technology). Isophorone does not dissolve polyethylene, polypropylene, polyamides, and polyurethanes (141).

Isophorone has also been suggested as an effective woodpecker repellant when coated onto telephone poles.

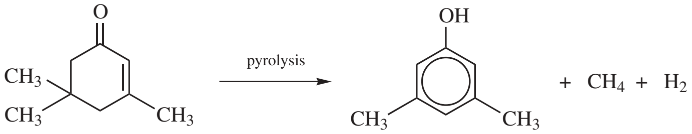
A trend in the utility of isophorone is as an important industrial building block. Foremost among these developments has been the use of isophorone as a raw material to produce isophorone diisocyanate (IPDI) [2855-13-2] for the production of light-stable polyurethane. The global market of IPDI, ~20 kt/yr in 1998, was estimated to grow at a rate of 6–8%/yr (142).



In the multistep production of IPDI, isophorone is first converted to 3-cyano-3,5,5-trimethylcyclohexanone (143–147) and then hydrogenated and ammoniated to 3-aminomethyl-3,5,5-trimethyl-1-aminocyclohexane (148,149), also known as isophorone diamine (IPDA) [2855-13-2]. In the final step, IPDA is phosgenated to yield IPDI (150). Commercial production of IPDI began in the United States in 1992 with the startup of Olin's 7 kt/yr plant at Lake Charles, Louisiana (151) and the start-up of the Hüls integrated isophorone derivatives plant in Theodore, Alabama (152). Olin's IPDI business has been traded several times and is currently owned by Bayer. Hüls IPDI business now belongs to its specialty chemicals subsidiary Creanova.

Creanova also markets an isophorone-derived aliphatic diisocyanate, trimethylhexamethylene diisocyanate (TMDI), which is composed of a mixture of 2,2,4- and 2,4,4-trimethylhexamethylene diisocyanate (153). This product is formed from isophorone by hydrogenating the unsaturation, forming an oxime of the resulting saturated ketone, performing a Beckmann rearrangement to obtain two isometric lactams, generating the aliphatic diamines by reductive ammination, and finally reaction with phosgene to yield the diisocyanates (154). A number of production processes for other isophorone derivatives are reported in the literature (68).

Isophorone can be selectively hydrogenated across the unsaturated double bond to yield 3,3,5-trimethylcyclohexanone [873-94-9] (154–156). A distillative hydrogenation process is reported (68,157). The saturated ketone is used as a solvent and as an intermediate in the preparation of peroxide polymerization initiators (141,158). Complete hydrogenation of isophorone gives 3,3,5-trimethylcyclohexanol [116-02-9]. This alcohol can exist in two stereoisomeric forms, which can be produced in various ratios depending on the reaction conditions. 3,3,5-Trimethylcyclohexanol can be used as a fragrance (159) and is used in the manufacture of vasodilator drugs by esterification with mandelic acid (160–162). Isophorone can be used to manufacture 3,5-xylenol [108-68-9] by catalytically aromatizing isophorone at 500–650°C (98,163–168). Rutgerswerke operates a process to produce crude 3,5-xylenol at temperatures of 520–540°C and pressures from 1 to 1.5 MPa (169).



3,5-Xylenol serves as an important starting material for insecticides, xylenol–formaldehyde resins, disinfectants, wood preservatives, and for the synthesis of α-tocopherol (vitamin E) (170) and dl-α-tocopherol acetate. The Bayer insecticide Methiocarb is manufactured by reaction of 3,5-xylenol with methylsulfenyl chloride to yield 4-methylmercapto-3,5-xylenol, followed by reaction with methyl isocyanate (169). Disinfectants and preservatives are produced by chlorination to 4-chloro- and 2,4-dichloro-3,5-dimethylphenol (163).

The catalytic oxidation of isophorone (171–173) or β-isophorone (174,175) to ketoisophorone [1125-21-9] (2,6,6-trimethyl-2-cyclohexen-1,4-dione) has been reported. Ketoisophorone is a building block for synthesis in terpene chemistry and for producing compounds of the vitamin A and E series.

*Health and Safety Factors.* Isophorone is considered moderately toxic by ingestion and skin contact (see Table 4). Some rat tumor formation evidence has been found (176), but no demonstration of human carcinogenicity has been presented. Isophorone is mildly toxic by inhalation, but because of its low volatility it is not a serious vapor hazard. In the United States, isophorone is considered an EPA priority pollutant under the CWA (see Table 6); it has a permissible acute toxicity concentration of 117 mg/L to protect freshwater aquatic life, 12.9 mg/L to protect saltwater aquatic life, and 5.2 mg/L to protect human life (177).

**7.2. Mesityl Oxide.** Mesityl oxide [141-79-7] (4-methyl-3-penten-2-one) is an oily colorless liquid with an unpleasant odor. It exhibits the versatility and unusual reactivity associated with conjugated α,β-unsaturated carbonyl compounds (178). On standing in air, mesityl oxide slowly forms bis(3,5,5-trimethyl-1,2-dioxolanyl)-3-peroxide (179).

Commercial mesityl oxide can contain 5–20% of the β,γ-unconjugated isomer isomesityl oxide [3744-02-3] (4-methyl-4-pentene-2-one). At equilibrium, the mixture contains 91% of the α,β-mesityl oxide and 9% of the β,γ-isomer (180–182). Isomerization is catalyzed by either acid or alkali. Techniques to isolate the isomers have been reported (180,182).

*Manufacture.* Mesityl oxide is produced by the liquid-phase dehydration of diacetone alcohol in the presence of acidic catalysts at 100–120°C and atmospheric pressure. As a precursor to MIBK, mesityl oxide is prepared in this manner in a distillation column in which acetone is removed overhead and water-saturated mesityl oxide is produced from a sidedraw. Suitable catalysts are phosphoric acid (183,184) and sulfuric acid (185,186). The kinetics of the reaction over phosphoric acid have been reported (187).

Mesityl oxide can also be produced by the direct condensation of acetone at higher temperatures. This reaction can be operated in the vapor phase over zinc oxide (188), or zinc oxide–zirconium oxide (189), or in the liquid phase over cation-exchange resin (190) or zirconium phosphate (191). Other catalysts are known (98).

*Health and Safety Factors.* Mesityl oxide is more toxic than saturated ketones and is highly irritating to all tissues on vapor or liquid contact (see Table 4). For this reason, sales of mesityl oxide ceased in the United States in 1986. It is absorbed through skin, and prolonged exposure can damage liver, kidneys, and lungs. Repeated exposure to vapors can cause anemia and leukopenia (192); however, the odor is so intolerable that long-term exposure is unlikely. Mesityl oxide is still produced, but is consumed captively as an intermediate in the production of MIBK, methyl isobutyl carbinol, and isophorone.

### 7.3. Methyl Vinyl Ketone.

Methyl vinyl ketone [78-94-4] (3-buten-2-one) is a colorless liquid with a pungent odor. It is stable only <0°C and readily polymerizes on standing at room temperature. It can be inhibited for storage and transportation by a mixture of acetic or formic acid and hydroquinone or catechol (193). This ketone is fairly soluble in water, and forms a binary azeotrope with water at 76°C (see Table 3).

Methyl vinyl ketone can be produced by the reactions of acetone and formaldehyde to form 4-hydroxy-2-butanone, followed by dehydration to the product (194,195). It can also be produced by the Mannich reaction of acetone, formaldehyde, and diethylamine (196). Its preparation via the oxidation of saturated alcohols or ketones such as 2-butanol and methyl ethyl ketone is also known (197). In addition, older patents report the synthesis of methyl vinyl ketone by the hydration of vinylacetylene (198,199).

Methyl vinyl ketone is used as a comonomer in photodegradable plastics, and is an intermediate in the synthesis of steroids and vitamin A. It is highly toxic and facilities in the United States handling over a threshold of 100 lb (45.5 kg) are subject to special OSHA documentation regulations (200).

### 7.4. Methyl Isopropenyl Ketone.

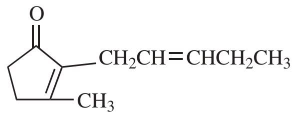
Methyl isopropenyl ketone [814-78-8] (3-methyl-3-buten-2-one) is a colorless, lachrymatory liquid, which like methyl vinyl ketone readily polymerizes on exposure to heat and light. It is produced via the condensation of MEK and formaldehyde over an acid cation-exchange resin at 130°C and 1500 kPa (14.8 atm) (201). Other methods are possible (202–207). Methyl isopropenyl ketone can be used as a comonomer to promote photochemical degradation in polymeric materials.

## 8. Cyclic Ketones

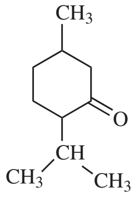
Cycloaliphatic ketones are colorless liquids with boiling points increasing regularly with molecular weight. Physical properties are given in Table 8. In addition, virtually all members of the series exhibit a characteristic odor depending on the ring size (208).

| Ring size | Odor |
|---|---|
| 5 | bitter almonds |
| 6 | peppermint |
| 7–9 | transition to camphor like |
| 10–12 | camphor like |
| 13 | cedar wood like |
| 14 | musklike |

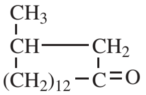
Many cyclic ketones occur in natural oils. Jasmone [488-10-8] (3-methyl-2-(2-pentyl)-2-cyclopenten-1-one) is an odoriferous component of the oil obtained from jasmine flowers. ℓ-Menthone [14073-97-3] is the most frequently occurring of four optically active isomers, and is a colorless liquid with a minty odor obtained from Mentha species of plants. Muscone [541-91-3] and civetone [542-46-1] are expensive animal products.



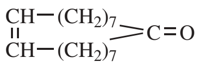
(**4**)



*l*-menthone

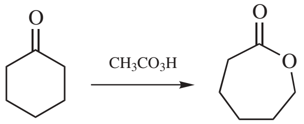


muscone



civetone

The chemical properties of cyclic ketones also vary with ring size. Lower members ($<C_8$) are more reactive, eg, toward addition reactions, than corresponding acyclic ketones. The $C_8$–$C_{12}$ ketones are unreactive, reflecting the strain and high enol content of medium-sized ring systems. Lactones are prepared from cyclic ketones by the Baeyer–Villiger oxidation reaction with peracids. ε-Caprolactone is manufactured from cyclohexane by this process:



Some toxicological data for cyclic ketones can be found in Table 4 for the two most common members and elsewhere for others (213). Interestingly, their toxicity appears to increase with ring size, in reverse order of their reactivity.

Cyclohexanone is by far the most important industrial cyclic ketone and is primarily used in the manufacture of $\gamma$-caprolactam as a precursor for nylon-6 (see CYCLOHEXANOL AND CYCLOHEXANONE).

## 9. Aromatic Ketones

Aromatic ketones of industrial significance include acetophenone, propiophenone, and benzophenone.

**9.1. Acetophenone.** Acetophenone [98-86-2] (methyl phenyl ketone) is a colorless liquid that forms laminar crystals at low temperature (mp 20°C). It has a characteristic sweet orange blossom odor and is soluble in alcohols and ethers. It is found in nature in oil of casatoreum, obtained from beavers; oil of labdanum, recovered from plants; and in buds of balsam poplar. It can be prepared by the Friedel–Crafts reaction of acetyl chloride with benzene in the presence of aluminum chloride; however, this route is of little commercial significance.

Sales demand for acetophenone is largely satisfied through distillative by-product recovery from residues produced in the Hock process for phenol manufacture. Acetophenone is produced in the Hock process by decomposition of cumene hydroperoxide. A more selective synthesis of acetophenone, by cleavage of cumene hydroperoxide over a cupric catalyst, has been patented (214). Acetophenone can also be produced by oxidizing the methylphenylcarbinol intermediate that is formed in styrene production processes using ethylbenzene oxidation, such as the ARCO and Halcon process and older technologies (215,216).

Acetophenone can react with formaldehyde to yield light-resistant resins that are used as additives in nitrocellulose paints. It is also used as a photoinitiator, and in the pharmaceuticals, perfumery, and pesticide industries (217). It can be hydrogenated to 1-phenylethanol, which is used for the production of aromatic ester fragrances (218).

**9.2. Propiophenone.** Propiophenone [93-55-0] (ethyl phenyl ketone) is a colorless liquid with a flowery odor. It can be prepared by the Friedel–Crafts reaction of benzene and propionyl chloride in the presence of aluminum chloride (219), or by the catalytic reaction of benzoic acid and propionic acid in the presence of water (220). Propiophenone is used in the production of ephedrine, as a fragrance enhancer, and as a polymerization sensitizer.

**9.3. Benzophenone.** Benzophenone [119-61-9] (diphenyl ketone) exists in a stable form as colorless orthorhombic bisphenoidal prisms when crystallized from alcohol or ether. Other labile forms of lower melting point exist. Benzophenone has been identified as a flavor component of wine grapes and has a geranium-like odor. It is soluble in most organic solvents and insoluble in water.

Benzophenone is produced by the oxidation of diphenylmethane (221). This (free-from-chlorine) (FCC) route is favored for perfume uses. The Friedel–Crafts reaction of benzene and benzoyl chloride in the presence of aluminum chloride is also possible; this reaction may proceed in the absence of catalyst at a temperature of 370°C and pressure of 1400 kPa (222).

Benzophenone is used as a photoinitiator in ultraviolet (u/v)-curable printing inks, coatings, and adhesive formulations, as a uv light-absorbing agent in personal care products, and as a perfume and flavor enhancer. It is also used as an intermediate for agricultural and pharmaceutical chemicals, eg, in the production of benzophenone hydrazone, a blocking agent used in the manufacture of penicillin (223).

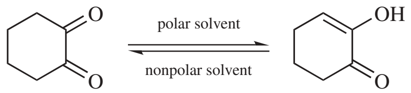
## 10. Diketones

Diketones contain two carbonyl groups and are named by adding the suffix "-dione" to the parent hydrocarbon and indicating the position of the carbonyl groups using the smallest numbers possible. Diketones are generally used as specialty chemical intermediates in the pharmaceutical, flavor, fragrance, and dye industries.

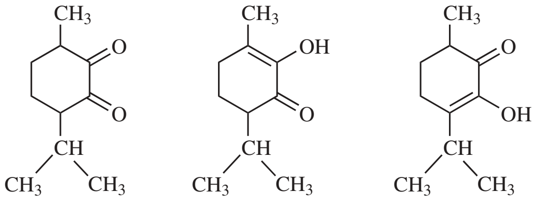
### 10.1. 1,2-Diketones.

α-Diketones contain two adjacent nonterminal carbonyl groups. Aliphatic 1,2-diketones are yellow liquids that possess a sharp, penetrating odor. In a diluted form they display a sweet, aromatic odor and are used in flavor formulations. Their boiling points increase with molecular weight, though the presence of branched chains tends to reduce the boiling point. The first few members of the series (eg, 2,3-butanedione, 2,3-hexanedione), are soluble in water; thereafter, increasing molecular weight reduces water solubility rapidly. Most cyclic and aromatic 1,2-diketones are yellow solids, and are almost odorless. Physical properties of representative 1,2-diketones are given in Table 9.

Cyclic 1,2-diketones demonstrate enolic tautomerism, with solvent polarity affecting tautomeric equilibrium:



Diosphenol [490-03-9], the main constituent of buchu leaves, is an example of a naturally occurring compound with tautomeric properties (227):



1,2-Diketones can be prepared by oxidation of the corresponding monoketone (228) or α-hydroxyketone (229). 1,2-Diketones are used extensively as intermediates in the preparation of pharmaceuticals, flavors, and fragrances.

***Biacetyl.*** Biacetyl [431-03-8] (2,3-butanedione) is a greenish yellow liquid with a quinone odor. Biacetyl occurs naturally in bay oil and is readily soluble in organic solvents. It is a constituent of many food aromas, eg, butter, and is commonly used to flavor margarine. It is also used as an odorant for coffee, vinegar, tobacco, and in perfumes.

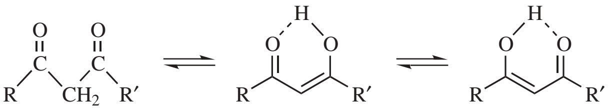
Biacetyl is produced by the dehydrogenation of 2,3-butanediol with a copper catalyst (230,231). Prior to the availability of 2,3-butanediol, biacetyl was prepared by the nitrosation of methyl ethyl ketone and the hydrolysis of the resultant oxime. Other commercial routes include passing vinyl acetylene into a solution of mercuric sulfate in sulfuric acid and decomposing the insoluble product with dilute hydrochloric acid (232), by the reaction of acetal with formaldehyde (233), by the acid-catalyzed condensation of 1-hydroxyacetone with formaldehyde (234), and by fermentation of lactic acid bacterium (235–237). Acetoin [513-86-0] (3-hydroxy-2-butanone) is also coproduced in lactic acid fermentation.

*Benzil.* Benzil [134-81-6] (diphenylethanedione) is a yellow solid that crystallizes from alcohol in hexagonal prisms. Benzil can be prepared by the oxidation of benzoin [579-44-2] (2-hydroxy-2-phenylacetophenone) (238,239), which is itself prepared by the self-condensation of benzaldehyde (240). Benzil is commercially produced in Japan and is used as a uv resin curing sensitizer (241). It has also been suggested as a chigger repellant (242).

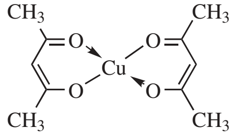
### 10.2. 1,3-Diketones.

β-Diketones contain two carbonyl groups separated by one carbon atom. Aliphatic 1,3-diketones are colorless liquids whose boiling point increases with increasing molecular weight, whereas cyclic 1,3-diketones are colorless solids. 1,3-Diketones are miscible with organic solvents, and lower molecular weight members have some water solubility. Many of the higher molecular weight members possess esterlike odors and are used in fragrances (243): 3-methyl-2,4-heptanedione [13152-54-0] with a fruity aroma, tetramethylcyclobutanedione [29714-52-3] with a minty smell, and benzoylacetone [93-91-4] with a balsamlike odor. Some physical properties of 1,3-diketones are shown in Table 10.

Because the 1,3-diketones comprise a methylene group that is structurally between two activating carbonyls, equilibrium is shifted toward the enol form. The equilibrium distribution varies with structure and solvent (243,246) (Table 11). The enol forms are cyclic and acidic and form covalent, colored, solid chelates with metals:



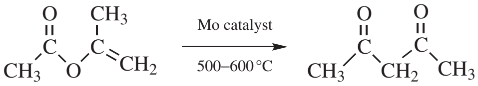
Ferric chelates produce red complexes and copper chelates produce blue or green complexes (Table 11). For bivalent metals, such as copper, the chelate structure of 2,4-pentanedione is as follows:



1,3-Diketones are used for extraction and identification of metals, and as raw materials for synthesis of heterocyclic compounds. The ability of 1,3-diketones to tie up essential metal ions in animal systems causes 1,3-diketones to be more toxic than other diketones.

*2,4-Pentanedione.* 2,4-Pentanedione [123-54-6] (acetylacetone) is the lowest member of the aliphatic 1,3-diketones and is a colorless liquid with a mild ketone-like odor. It is completely miscible with organic solvents.

The industrial precursor to 2,4-pentanedione is isopropenyl acetate, produced from acetone and ketene (247,248). The diketone is formed by the high temperature isomerization of isopropenyl acetate over a metal catalyst (249–251).



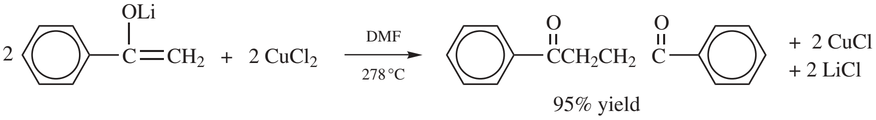
2,4-Pentanedione can also be produced by the condensation of acetone with ethyl acetate (252–257), or by the condensation of ethyl acetoacetate and ketene (258–261). Other methods are known (262,263).

2,4-Pentanedione is widely used in extraction processes for the separation and purification of metals because of its ability to form covalent metal chelates. It is also used as an intermediate in the production of heterocyclic substances and dyes, as a fuel additive (264), and in metal plating and resin modification.

The toxicity of 2,4-pentanedione is similar to mesityl oxide, and greater than most other 1,2- or 1,4-diketones or monoketones (see Table 4). Inhalation of low levels of 2,4-pentanedione can cause nausea, eye contact can induce stinging, and recurrent exposure to high concentrations (300–400 ppm) can adversely affect the central nervous system and immune system (6).

**10.3. 1,4-Diketones.** $\gamma$-Diketones contain two carbonyl groups separated by two carbon atoms. With the exception of 2,5-hexanedione, which is a high boiling liquid, 1,4-diketones are low melting white solids with only faint odors. Lower molecular weight members are soluble in organic solvents and water. Properties of representative 1,4-diketones are shown in Table 12.

1,4-Diketones are intermediates for synthesis of perfumes and natural products, and several preparative methods have been developed (266); in the simplest preparative methods, ketone enolates are oxidatively dimerized (267):



1,4-Diketones are readily transformed to cyclic derivatives, such as cyclopentanones and furans. In this manner, the fragrance dihydrojasmone (3-methyl-2-pentyl-2-cyclopenten-1-one) is prepared by the base-catalyzed aldol condensation of 2,5-undecanedione. 2,5-Undecanedione is itself prepared from heptanal and methyl vinyl ketone in the presence of thiazolium salts (268). cis-Jasmone can be similarly prepared (269,270).

2,5-Hexanedione [110-13-4] (acetonylacetone) is one of the most widely used 1,4-diketones. It is a colorless high boiling liquid prepared by the hydrolysis of

2,5-dimethylfuran (271,272), by oxidation of 2,5-hexanediol (273) or 5-hexen-1-one (274), and from allylacetone (275). Its main use is in solvent systems and as a raw material for chemical synthesis.

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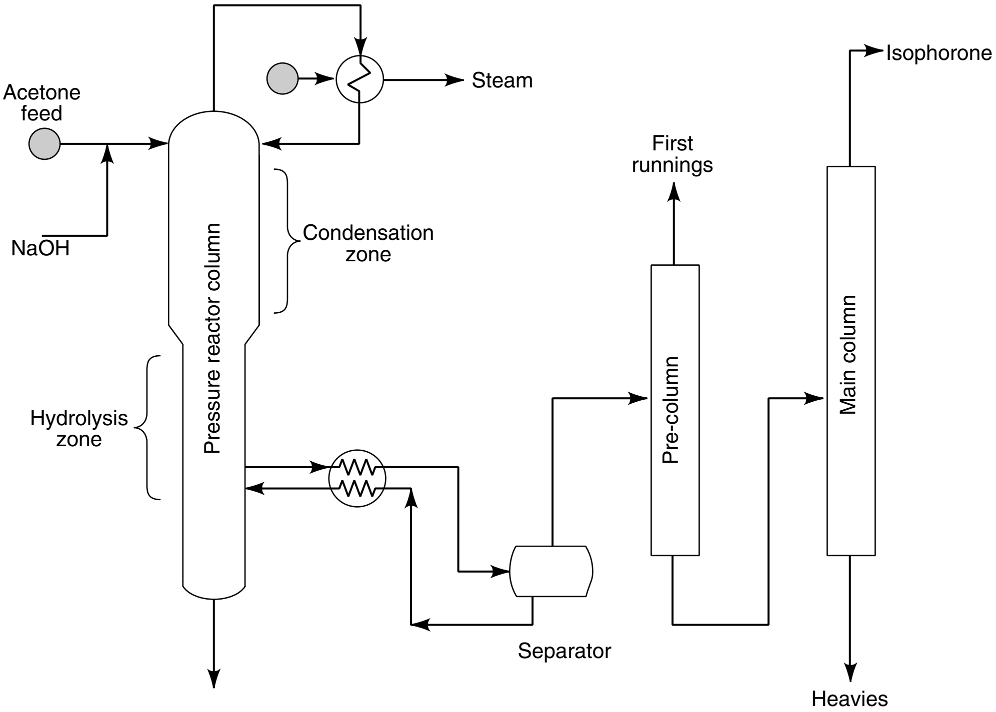

**Fig. 1.** Liquid-phase isophorone process (68). Courtesy of Chemische Industrie.

Table 1. **Common Ketones**

| Common name | Systematic name | Synonyms[a] | CAS Registry number | Formula |
|---|---|---|---|---|
| | | *Aliphatic ketones* | | |
| acetone | 2-propanone | propanone; dimethyl ketone; methyl ketone | [67-64-1] | $C_3H_6O$ |
| methyl ethyl ketone | 2-butanone | MEK; ethyl methyl ketone; butanone; methylacetone | [78-93-3] | $C_4H_8O$ |
| methyl propyl ketone | 2-pentanone | methyl *n*-propyl ketone; ethylacetone | [107-87-9] | $C_5H_{10}O$ |
| methyl isopropyl ketone | 3-methyl-2-butanone | MIPK; isopropyl methyl ketone | [563-80-4] | $C_5H_{10}O$ |
| diethyl ketone | 3-pentanone | DEK; ethyl ketone; propione; dimethylacetone | [96-22-0] | $C_5H_{10}O$ |
| methyl butyl ketone | 2-hexanone | MBK; methyl *n*-butyl ketone; butyl methyl ketone | [591-78-6] | $C_6H_{12}O$ |
| methyl isobutyl ketone | 4-methyl-2-pentanone | MIBK; hexone; isobutyl methyl ketone; isopropylacetone | [108-10-1] | $C_6H_{12}O$ |
| methyl *sec*-butyl ketone | 3-methyl-2-pentanone | *sec*-butyl methyl ketone | [565-61-7] | $C_6H_{12}O$ |
| methyl *tert*-butyl ketone | 3,3-dimethyl-2-butanone | *tert*-butyl methyl ketone; pinacolone | [75-97-8] | $C_6H_{12}O$ |
| ethyl propyl ketone | 3-hexanone | ethyl *n*-propyl ketone | [589-38-8] | $C_6H_{12}O$ |
| diacetone alcohol | 4-hydroxy-4-methyl-2-pentanone | acetonyldimethylcarbinol; diacetone; pyranton;tyranton | [123-42-2] | $C_6H_{12}O_2$ |
| methyl amyl ketone | 2-heptanone | MAK; methyl *n*-amyl ketone; amyl methyl ketone; methyl pentyl ketone | [110-43-0] | $C_7H_{14}O$ |
| methyl isoamyl ketone | 5-methyl-2-hexanone | MIAK: isoamyl methyl ketone; isopentyl methyl ketone | [110-12-3] | $C_7H_{14}O$ |
| ethyl butyl ketone | 3-heptanone | butyl ethyl ketone | [106-35-4] | $C_7H_{14}O$ |
| dipropyl ketone | 4-heptanone | propyl ketone; butyrone | [123-19-3] | $C_7H_{14}O$ |
| diisopropyl ketone | 2,4-dimethyl-3-pentanone | isopropyl ketone; isobutyrone | [565-80-0] | $C_7H_{14}O$ |
| methyl hexyl ketone | 2-octanone | | [111-13-7] | $C_8H_{16}O$ |
| ethyl amyl ketone | 3-octanone | amyl ethyl ketone | [106-68-3] | $C_8H_{16}O$ |
| diisobutyl ketone | 2,6-dimethyl-4-heptanone | isobutyl ketone; isovalerone | [108-83-8] | $C_9H_{18}O$ |
| isobutyl heptyl ketone | 2,6,8-trimethyl-4-nonanone | | [123-18-2] | $C_{12}H_{24}O$ |
| | | *Unsaturated ketones* | | |
| methyl vinyl ketone | 3-buten-2-one | methyleneacetone | [78-94-4] | $C_4H_6O$ |
| methyl isopropenyl ketone | 3-methyl-3-buten-2-one | isopropenyl methyl ketone | [814-78-8] | $C_5H_8O$ |
| mesityl oxide | 4-methyl-3-penten-2-one | methyl isobutenyl ketone;isobutenyl methyl ketone; isopropylidene acetone | [141-79-7] | $C_6H_{10}O$ |
| isomesityl oxide | 4-methyl-4-penten-2-one | | [3744-02-3] | $C_6H_{10}O$ |
| phorone | 2,6-dimethyl-2,5-heptadien-4-one | diisopropylidene acetone | [504-20-1] | $C_9H_{14}O$ |

Table 1 (*Continued*)

| Common name | Systematic name | Synonyms[a] | CAS Registry Number | Formula |
|---|---|---|---|---|
| isophorone | 3,5,5-trimethyl-2-cyclohexen-1-one | α-isophorone; isoacetophorone | [78-59-1] | $C_9H_{14}O$ |
| β-isophorone | 3,5,5-trimethyl-3-cyclohexen-1-one | | [471-01-2] | $C_9H_{14}O$ |
| | | *Cyclic ketones* | | |
| cyclopentanone | cyclopentanone | adipic ketone | [120-92-3] | $C_5H_8O$ |
| cyclohexanone | cyclohexanone | pimelic ketone; anone; nadone; sextone | [108-94-1] | $C_6H_{10}O$ |
| cycloheptanone | cycloheptanone | suberone | [502-42-1] | $C_7H_{12}O$ |
| | | *Aromatic ketones* | | |
| acetophenone | 1-phenyl-1-ethanone | methyl phenyl ketone; hypnone; acetylbenzene | [98-86-2] | $C_8H_8O$ |
| propiophenone | 1-phenyl-1-propanone | ethyl phenyl ketone; propionylbenzene | [93-55-0] | $C_9H_{10}O$ |
| phenylacetone | 1-phenyl-2-propanone | methyl benzyl ketone; benzyl methyl ketone | [103-79-7] | $C_9H_{10}O$ |
| benzophenone | diphenylmethanone | diphenyl ketone; phenyl ketone; benzoylbenzene | [119-61-9] | $C_{13}H_{10}O$ |
| | | *Diketones* | | |
| 2,3-butanedione | 2,3-butanedione | butanedione; biacetyl; diacetyl; dimethylglyoxal | [431-03-8] | $C_4H_6O_2$ |
| 2,3-pentanedione | 2,3-pentanedione | acetylpropionyl | [600-14-6] | $C_5H_8O_2$ |
| 2,4-pentanedione | 2,4-pentanedione | pentanedione; acetylacetone; acetoacetone | [123-54-6] | $C_5H_8O_2$ |
| 2,5-hexanedione | 2,5-hexanedione | acetonylacetone | [110-13-4] | $C_6H_{10}O_2$ |
| diphenylethanedione | diphenylethanedione | benzil; dibenzoyl; diphenylglyoxal | [134-81-6] | $C_{14}H_{10}O_2$ |

[a] Refs. 2 and 3.

Table 2. **Physical Properties of Common Ketones**[a]

| Common name | CAS Registry Number | Molecular weight | Melting point,[b] °C | Normal boiling point,[b] °C | Refractive index at 25°C[c] | Liquid density at 25°C,[c] g/mL | Liquid viscosity at 25°C,[c] cP | Surface tension at 25°C,[c] dyn/cm | Liquid heat capacity at 25°C,[c] J/g K | Heat of vaporization at NBP,[d] kJ/mol |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | *Aliphatic ketones* | | | | | |
| acetone | [67-64-1] | 58.080 | −94.7 | 56.3 | 1.3560 | 0.7866 | 0.307 | 23.0 | 2.175 | 29.56 |
| methyl ethyl ketone | [78-93-3] | 72.107 | −86.7 | 79.6 | 1.3764 | 0.7995 | 0.395 | 24.0 | 2.200 | 31.55 |
| methyl propyl ketone | [107-87-9] | 86.134 | −76.9 | 102.3 | 1.3880 | 0.8035 | 0.471 | 23.8 | 2.138 | 33.45 |
| methyl isopropyl ketone | [563-80-4] | 86.134 | −93.0 | 94.4 | 1.3857 | 0.7990 | 0.430 | 22.1 | 2.090 | 32.63 |
| diethyl ketone | [96-22-0] | 86.134 | −39.0 | 102.0 | 1.3900 | 0.8095 | 0.444 | 24.7 | 2.215 | 33.48 |
| methyl butyl ketone | [591-78-6] | 100.161 | −55.8 | 127.6 | 1.3987 | 0.8071 | 0.583 | 25.5 | 2.128 | 36.30 |
| methyl isobutyl ketone | [108-10-1] | 100.161 | −84.0 | 116.0 | 1.3933 | 0.7962 | 0.544 | 23.4 | 2.135 | 34.56 |
| methyl *sec*-butyl ketone | [565-61-7] | 100.161 | −106.0 | 117.4 | 1.3978 | 0.8078 | 0.583 | 23.8 | 2.084 | 34.97 |
| methyl *tert*-butyl ketone | [75-97-8] | 100.161 | −52.0 | 106.3 | 1.3943 | 0.8019 | 0.653 | 21.9 | 2.052 | 33.32 |
| ethyl propyl ketone | [589-38-8] | 100.161 | −55.7 | 123.5 | 1.3980 | 0.8104 | 0.578 | 25.0 | 2.163 | 35.63 |
| diacetone alcohol | [123-42-2] | 116.160 | −44.0 | 167.9 | 1.4219 | 0.9345 | 2.913 | 29.7 | 1.878 | 44.44 |
| methyl amyl ketone | [110-43-0] | 114.188 | −35.0 | 151.0 | 1.4066 | 0.8116 | 0.751 | 26.1 | 2.121 | 38.35 |
| methyl isoamyl ketone | [110-12-3] | 114.188 | −73.9 | 144.8 | 1.4047 | 0.8081 | 0.691 | 25.6 | 2.032 | 38.43 |
| ethyl butyl ketone | [106-35-4] | 114.188 | −39.0 | 147.4 | 1.4066 | 0.8139 | 0.743 | 25.7 | 2.152 | 38.49 |
| dipropyl ketone | [123-19-3] | 114.188 | −32.5 | 144.0 | 1.4045 | 0.8121 | 0.708 | 25.4 | 2.174 | 37.45 |
| diisopropyl ketone | [565-80-0] | 114.188 | −68.3 | 124.4 | 1.3976 | 0.8008 | 0.626 | 22.4 | 2.062 | 35.52 |
| methyl hexyl ketone | [111-13-7] | 128.214 | −20.3 | 173.0 | 1.4133 | 0.8151 | 0.924 | 25.9 | 2.126 | 40.74 |
| ethyl amyl ketone | [106-68-3] | 128.214 | | 167.5[e] | 1.4150 (20)[e] | 0.822[e] | | | | |
| diisobutyl ketone | [108-83-8] | 142.241 | −46.0 | 168.3 | 1.4123 | 0.8018 | 0.869 | 22.8 | | 39.57 |
| isobutyl heptyl ketone | [123-18-2] | 184.32[f] | −59.2[f] | 217.2[f] | 1.4257(20)[f] | 0.8188(20)[f] | 1.74[f] | 26.1[f] | | 44.56[f] |
| | | | | | *Unsaturated ketones* | | | | | |
| methyl vinyl ketone | [78-94-4] | 70.09[e] | −6[g] | 81.4[e] | 1.4081 (20)[e] | 0.8640 (20)[e] | | | | |
| methyl isopropenyl ketone | [814-78-8] | 84.118 | −53.6 | 98.0 | 1.4212 | 0.8462 | 0.397 | 25.3 | | 32.66 |
| mesityl oxide | [141-79-7] | 98.145 | −53.0 | 129.8 | 1.4414 | 0.8520 | 0.602 | 27.9 | 2.163 | 35.94 |
| isomesityl oxide | [3744-02-3] | 98.145 | −72.6[e] | 124.2[e] | 1.4213 (20)[h] | 0.8411(20)[e] | 0.634 (20)[h] | 23.0 (20)[h] | | 36.07[h] |
| phorone | [504-20-1] | 138.210 | 28.0[e] | 197.5[e] | 1.4998 (20)[e] | 0.8850 (20)[e] | | | | |
| isophorone | [78-59-1] | 138.210 | −8.1 | 215.2 | 1.4780 | 0.9196 | 2.329 | 31.2 | 1.834 | 42.37 |
| β-isophorone | [471-01-2] | 138.210 | | 186[g] | | 0.8884 (20)[g] | | | | |
| | | | | | *Cyclic Ketones* | | | | | |
| cyclopentanone | [120-92-3] | 84.118 | −51.3 | 130.7 | 1.4347 | 0.9442 | 1.071 | 32.9 | 1.781 | 36.40 |
| cyclohexanone | [108-94-1] | 98.145 | −31.2 | 155.4 | 1.4499 | 0.9428 | 2.015 | 34.4 | 1.888 | 38.06 |
| cycloheptanone | [502-42-1] | 112.17[e] | −21[g] | 178.5[e] | 1.4608 (20)[e] | 0.9508 (20)[e] | | 26.4 | | |

Table 2 (*continued*)

| Common name | CAS Registry Number | Molecular weight | Melting point,[b] °C | Normal boiling point,[b] °C | Refractive index at 25°C[c] | Liquid density at 25°C,[c] g/mL | Liquid viscosity at 25°C,[c] cP | Surface tension at 25°C,[c] dyn/cm | Liquid heat capacity at 25°C,[c] J/g K | Heat of vaporization at NBP,[d] kJ/mol |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | *Aromatic Ketones* | | | | | | |
| acetophenone | [98-86-2] | 120.151 | 19.7 | 202.1 | 1.5321 | 1.0234 | 1.645 | 39.0 | 1.706 | 44.06 |
| propiophenone | [93-55-0] | 134.18[e] | 18.6[e] | 217.5[e] | 1.5269 (20)[e] | 1.0096 (20)[e] | | 37.4 (20)[e] | | 45.48[f] |
| phenylacetone | [103-79-7] | 134.18[e] | −15.0[e] | 216.5[e] | 1.5168 (20)[e]<br>(20)[e] | 1.0157 (20)[e]<br>(20)[e] | | | | |
| benzophenone | [119-61-9] | 182.222 | 48.2 | 306.1 | 1.5975 | 1.0840 | | | | 54.29 |
| | | | | *Diketones* | | | | | | |
| 2,3-butanedione | [431-03-8] | 86.09[e] | −2.4[e] | 88[e] | 1.3951 (20)[e] | 0.9818 (18)[e] | | | | 34.3[g] |
| 2,3-pentanedione | [600-14-6] | 100.117 | | 108[e] | 1.4014 (19)[e]<br>(19)[e] | 0.9565 (19)[e]<br>(19)[e] | | 31 (20)[g]<br>(20)[g] | 1.983 (20)[g]<br>(20)[g] | 35.4[g] |
| 2,4-pentanedione | [123-54-6] | 100.117 | −23.2 | 140.4 | 1.4465 | 0.9711 | 0.767 | 30.4 | 2.080 | 35.88 |
| 2,5-hexanedione | [110-13-4] | 114.14[e] | −5.5[e] | 194[e] | 1.4232 (20)[e]<br>(20)[e] | 0.9717 (20)[i]<br>(20)[i] | 1.6 (20)[i]<br>(20)[i] | | 1.958 (20)[i]<br>(20)[i] | 36.6[i] |
| diphenylethanedione | [134-81-6] | 210.23[e] | 94.8[e] | 347[e] | | 1.0840 (102)[e]<br>(102)[e] | | | | |

[a] Data are obtained from Ref. 2 unless otherwise noted (see notes *e*–*i*).

[b] At 1 atm (101.3 kPa).

[c] Values at temperatures other than 25°C are noted with the temperature in parentheses. For the data from Ref. 2, the liquid viscosity, surface tension, and liquid heat capacity at 25°C are calculated from the temperature correlations.

[d] NBP = normal boiling point (at 1 atm = 101.3 kPa). For the data from Ref. 2, the heat of vaporization at NBP are calculated from the temperature correlations.

[e] Ref. 4.

[f] Ref. 6.

[g] Ref. 7.

[h] Ref. 5.

[i] Ref. 8.

Table 3. **Ketone−Water Mixture Properties for Common Ketones**

| | | Solubility at 25°C,[a] | | Binary azeotrope at 1 atm (101.3 kPa)[b] | | | Henry's law constant at 25°C,[c] atm/mol fr | |
|---|---|---|---|---|---|---|---|---|
| Common name | CAS Registry Number | Ketone in water | Water in ketone | Type (P, kPa)[d] | Boiling point (ketone)[e], °C | Composition, wt% ketone | EPA (CMA rev.)[f] | Calculated (vp) (ac)[g] |
| | | *Aliphatic ketones* | | | | | | |
| acetone | [67-64-1] | miscible | miscible | min (687.4) | 124.1 (125.4) | 97.0 | n/d (1.85) | 2.1 |
| methyl ethyl ketone | [78-93-3] | 24.8 | 11.5 | min | 73.4 | 88.7 | 7.22 (13.5) | 2.1 |
| methyl propyl ketone | [107-87-9] | 5.49 | 3.48 | het | 83.3 | 80.5 | 3.47 | 3.3 |
| methyl isopropyl ketone | [563-80-4] | 5.88 | 2.57 | het | 79.0 | 87.0 | 25.4 | 4.7 |
| diethyl ketone | [96-22-0] | 4.83 | 1.69 | het | 82.9 | 76.0 | 2.78 | 4.3 |
| methyl butyl ketone | [591-78-6] | 1.59 | 2.24 | het | 90.5 | 69.7 | | 4.7 |
| methyl isobutyl ketone | [108-10-1] | 1.88 | 1.96 | het | 87.9 | 75.7 | 25.3 | 6.9 |
| methyl *sec*-butyl ketone | [565-61-7] | 2.09 | 2.02 | | | | | 5.9 |
| methyl *tert*-butyl ketone | [75-97-8] | 1.90 | 1.76 | het | 85.0 | 85.5 | | 11 |
| ethyl propyl ketone | [589-38-8] | 1.47 | 1.62 | | | | | 6.2 |
| diacetone alcohol | [123-42-2] | miscible[h] | miscible[h] | min | 98.8 | 12.7 | | 0.035 |
| methyl amyl ketone | [110-43-0] | 0.430 | 1.41 | het[i] | 95.0 | | 0.794 | 6.9 |
| methyl isoamyl ketone | [110-12-3] | 0.54(20)[j] | 1.28(20)[j] | het[k] | 94.7 | 56.0 | 7.0 (99.4) | 7.4 |
| ethyl butyl ketone | [106-35-4] | 1.43(20)[l] | 0.78(20)[l] | het[k] | 94.6 | 57.8 | | 2.3 |
| dipropyl ketone | [123-19-3] | 0.382(30) | | het[k] | 94.3 | 59.5 | | 13 |
| diisopropyl ketone | [565-80-0] | 0.570 | 0.810 | | | | n/d (31.6) | 12 |
| methyl hexyl ketone | [111-13-7] | 0.113[l] | | | | | 10.3 | 12 |
| diisobutyl ketone | [108-83-8] | 0.090 | 0.549 | het[k] | 97.0 | 48.1 | | 19 |
| isobutyl heptyl ketone | [123-18-2] | <0.5(20)[h] | 0.2(20)[h] | het[k] | 99.0 | 16.0 | | 17 |
| | | *Unsaturated ketones* | | | | | | |
| methyl vinyl ketone | [78-94-4] | 47.2(30) | 34.1(30) | min (99.1)[i] | 75.5 (81.0) | 85.8 | 1.36 | 1.2 |
| methyl isopropenyl ketone | [814-78-8] | | | min[l] | 81.5 | 81.6 | | |
| mesityl oxide | [141-79-7] | 2.89(20)[l] | 2.85(20)[l] | het | 91.8 | 65.2 | | 2.3 |
| isophorone | [78-59-1] | 1.2(20)[h] | 4.3(20)[h] | het[k] | 99.5 | 16.1 | 0.368 (0.284) | 0.27 |
| | | *Cyclic ketones* | | | | | | |
| cyclopentanone | [120-92-3] | 29(20)[j] | 14(20)[j] | het[k] | 94.6 | 57.6 | | 0.41 |
| cyclohexanone | [108-94-1] | 9.31 | 5.94 | het[k] | 96.3 | 45.0 | | 0.21 |
| cycloheptanone | [502-42-1] | 0.3(20)[j] | 1.4(20)[j] | | | | | |
| | | *Aromatic ketones* | | | | | | |
| acetophenone | [98-86-2] | 0.683 | 1.45 | het[k] | 99.1 | 18.5 | 0.509 | 0.46 |
| propiophenone | [93-55-0] | 0.2(20)[h] | 1.0(20)[h] | | | | | 2.6 |
| benzophenone | [119-61-9] | | | | | | 506 | |

Table 3 (*Continued*)

| Common name | CAS Registry Number | Solubility at 25°C,[a] | | Binary azeotrope at 1 atm (101.3 kPa)[b] | | | Henry's law constant at 25°C,[c] atm/mol fr | |
|---|---|---|---|---|---|---|---|---|
| | | Ketone in water | Water in ketone | Type (P, kPa)[d] | Boiling point (ketone)[e], °C | Composition, wt% ketone | EPA (CMA rev.)[f] | Calculated (vp) (ac)[g] |
| | | | | *Diketones* | | | | |
| 2,3-butanedione | [431-03-8] | | | het[i] | 78.5 | 81.7 | | |
| 2,3-pentanedione | [600-14-6] | | | het | 86.0 | | | |
| 2,4-pentanedione | [123-54-6] | 14.5 | 4.49 | het[k] | 94.4 | 59.0 | | 0.48 |

[a] Solubilities are obtained from Ref. 9 unless otherwise noted (see notes *h*–*j* and *l*). Values at temperatures other than 25°C are noted with the temperature in parentheses.

[b] Azeotrope data are obtained from Ref. 10 unless otherwise noted in the Type column (see notes *i* and *k*).

[c] Henry's law constants are mostly indirectly measured or estimated to only order-of-magnitude accuracy.

[d] Azeotrope types: min = homogeneous minimum boiling; het = heterogeneous minimum boiling. Azeotropes at pressures other than 101.3 kPa are noted with the pressures in parentheses.

[e] For an azeotrope at a pressure other than 101.3 kPa, the boiling point of the ketone at that pressure is given in parentheses. For the boiling points of ketones at 101.3 kPa, see Table 2.

[f] Values from a tentative databank of U.S. Environmental Protection Agency (EPA) with revised values from Chemical Manufacture Association (CMA) in parentheses (Ref. 13); n/d = no data in the tentative EPA databank.

[g] Values calculated from vapor pressure (vp) computed with temperature correlations from Ref. 2 and infinite-dilution activity coefficient (ac) estimated from either solubilities or vapor–liquid equilibrium data with the estimation methods from Ref. 14.

[h] Ref. 6.

[i] Ref. 11.

[j] Ref. 7.

[k] Ref. 12.

[l] Ref. 5.

Table 4. **Commercial Information for Industrial Ketones**

| Common name | CAS Registry number | Price[a] US$/kg | Major producer[b] | Plant location[b] | Capacity (1999),[b] kt/yr |
|---|---|---|---|---|---|
| | | | *Aliphatic ketones* | | |
| acetone[c] | [67-64-1] | 0.36 | Sunoco | Pa., USA | 282 |
| | | | Aristech Chemical | Ohio, USA | 268 |
| | | | General Electric | Ind., USA | 198 |
| | | | Shell Chemical | Tex., USA | 191 |
| | | | Georgia Gulf | La./Tex., USA | 186 |
| | | | Dow Chemical | Tex., USA | 182 |
| methyl ethyl ketone[d] | [78-93-3] | 1.01 | Shell Chemical | La., USA | 136 |
| | | | Exxon Chemical | La., USA | 135 |
| | | | Exxon Chemical | UK | 135 |
| | | | Shell Nederland Chemie BV | Holland | 85 |
| | | | Maruzen Petrochemical | Japan | 90 |
| | | | Tonen Chemical | Japan | 70 |
| methyl isopropyl ketone | [563-80-4] | | Eastman Chemical | Tenn., USA | |
| | | | BASF Aktiengesellschaft | Germany | |
| | | | Condea Chemie GmbH | Germany | |
| | | | Chisso Petrochemical | Japan | |
| | | | Kuraray Co. | Japan | |
| | | | Jilin Chemical | Jilin, China | |
| diethyl ketone | [96-22-0] | | Union Carbide[e] | W.V., USA | |
| | | | BASF Aktiengesellschaft | Germany | |
| | | | Esperis SpA | Italy | |
| | | | Industrie Chimiche Caffaro SpA | Italy | |
| | | | Chisso Corp. | Japan | |
| | | | Siegfried Chemicals | Taiwan | |
| methyl isobutyl ketone[f] | [108-10-1] | 1.43 | Shell Chemical | Tex., USA | 45 |
| | | | Union Carbide[e] | W.V., USA | 34 |
| | | | Shell Nederland Chemie BV | Holland | 45 |
| | | | Shell Chimie S.A. | France | 25 |
| | | | Societa Italiana Serie Acetica Sintetica SpA | Italy | 25 |
| | | | Mitsui Chemicals | Japan | 22 |
| | | | Mitsubishi Chemical | Japan | 20 |
| | | | Lee Chang Yung Chemical Industry Corp. | Taiwan | 20 |

Table 4. (*Continued*)

| Common name | CAS Registry number | Price[a] US$/kg | Major producer[b] | Plant location[b] | Capacity (1999),[b] kt/yr |
|---|---|---|---|---|---|
| diacetone alcohol | [123-42-2] | 1.32 | Shell Chemical | Tex., USA | |
| | | | Celanese | Tex., USA | |
| | | | Celanese Mexicana, S.A. de C.V. | Mexico | |
| | | | Rhodia S.A. | Brazil | |
| | | | Societa Italiana Serie Acetica Sintetica SpA | Italy | |
| | | | BP Chemicals | UK | |
| | | | Elf Atochem SA | France | |
| | | | Shell Chimie S.A. | France | |
| | | | Shell Nederland Chemie BV | Holland | |
| | | | Mitsubishi Chemical | Japan | |
| methyl amyl ketone | [110-43-0] | 1.71 | Eastman Chemical | Tenn., USA | |
| | | | Chemie Uetikon GmbH | Germany | |
| | | | Suchema AG | Switzerland | |
| | | | Danisco Ingredients | Denmark | |
| methyl isoamyl ketone | [110-12-3] | 1.64 | Eastman Chemical | Tenn., USA | |
| | | | BASF Aktiengesellschaft | Germany | |
| | | | Chemie Uetikon GmbH | Germany | |
| diisobutyl ketone | [108-83-8] | 1.80 | Union Carbide[e] | W.V., USA | |
| | | | Eastman Chemical | Tenn., USA | |
| | | | Sol Petroleo S.A. | Argentina | |
| | | | Tsau Hin Resin Enterprise | Taiwan | |
| isobutyl heptyl ketone | [123-18-2] | | Union Carbide[e] | W.V., USA | |
| *Unsaturated ketones* | | | | | |
| methyl vinyl ketone | [78-94-4] | | Arran Chemical | Ireland | |
| methyl isopropenyl ketone | [814-78-8] | | CONDEA Chemie GmbH | Germany | |
| mesityl oxide | [141-79-7] | | Celanese Mexicana, S.A. de C.V. | Mexico | |
| | | | Rhodia S.A. | Brazil | |
| | | | Elf Atochem SA | France | |
| isophorone | [78-59-1] | 1.87 | Creanova Spezialchemie GmbH | Ala., USA | 25 |
| | | | Union Carbide[e] | W.V., USA | 11 |

Table 4. (*Continued*)

| Common name | CAS Registry number | Price[a] US$/kg | Major producer[b] | Plant location[b] | Capacity (1999),[b] kt/yr |
|---|---|---|---|---|---|
| | | | Creanova Spezialchemie GmbH | Germany | 52 |
| | | | Elf Atochem SA | France | 38 |
| | | | Societa Italiana Serie Acetica Sintetica SpA | Italy | 9 |
| | | | BP Chemicals | UK | 6 |
| | | | Daicel Chemical Industries | Japan | |
| | | | *Cyclic ketones* | | |
| cyclohexanone[g] | [108-94-1] | 1.61 | DuPont Specialties | Tex./Tex., USA | 548 |
| | | | Allied Signal | Va., USA | 327 |
| | | | DSM Chemicals | Ga., USA | 320 |
| | | | BASF | Tex., USA | 232 |
| | | | *Aromatic ketones* | | |
| acetophenone | [98-86-2] | 7.70 | Penta Manufacturing Co. | N.J., USA | |
| | | (perfume | Rhodia S.A. | Brazil | |
| | | grade, | Haarmann & Reimer GmbH | Germany | |
| | | 25 kg) | Jilin City Petrochemical Industry Co. | Jilin, China | |
| propiophenone | [93-55-0] | | Industrie Chimiche Caffaro SpA | Italy | |
| | | | Daicel Chemical Industries. | Japan | |
| | | | Matsugaki Chemical Industries | Japan | |
| | | | Siegfried Chemicals | Taiwan | |
| benzophenone | [119-61-9] | 6.60 | Sartomer | Pa., USA | |
| | | (technical | Velsicol Chemical | Ill., USA | |
| | | grade, | Warner-Lambert | Mich., USA | |
| | | 200 kg) | Witco Mexico, S.A. de C.V. | Mexico | |
| | | | Haarmann & Reimer GmbH | Germany | |
| | | | A & E Connock | UK | |
| | | | Elf Atochem UK | UK | |
| | | | Industrie Chimiche Caffaro SpA | Italy | |
| | | | Matsugaki Chemical Industries Co. | Japan | |
| | | | Toyo Kasei Kogyo Co. | Japan | |

Table 4. (*Continued*)

| Common name | CAS Registry number | Price[a] US$/kg | Major producer[b] | Plant location[b] | Capacity (1999),[b] kt/yr |
|---|---|---|---|---|---|
| | | | *Diketones* | | |
| 2,3-butanedione | [431-03-8] | | Penta Manufacturing Co. | N.J., USA | |
| | | | BASF Mexicana, S.A. de C.V. | Mexico | |
| | | | Oxford Chemicals | UK | |
| | | | BASF Aktiengesellschaft | Germany | |
| | | | Haarmann & Reimer GmbH | Germany | |
| | | | Usines Lambiotte S.A. | France | |
| | | | Royal Gist-brocades NV | Holland | |
| 2,4-pentanedione | [123-54-6] | | Union Carbide[e] | W.V., USA | |
| | | | Penta Manufacturing Co. | N.J., USA | |
| | | | Wacker-Chemie GmbH | Germany | |
| | | | Daicel Chemical Industries | Japan | |
| | | | Shandong Weifang Tianhe Organic Chemical | Shandong, China | |
| | | | Shanghai Chemical Raw Materials Co. | Shanghai, China | |
| diphenylethanedione | [134-81-6] | | Schweizerhall | N.J., USA | |
| | | | Industrie Chimiche Caffaro SpA | Italy | |
| | | | Katwijk Chemie BV | Holland | |
| | | | Kurogane Kasei Co. | Japan | |

[a] U.S. market price for tank quantity (unless otherwise noted) in March 2000 from Ref. 18 (converted from \$/lb).

[b] Most producer data are from Ref. 49, Courtesy of SRI International, unless otherwise noted (see notes *c–e*); for capacity, kt = kiloton (metric) = 2.2 million lb.

[c] Producer data for acetone are from Ref. 20; only major U.S. producers are listed.

[d] Producer data for methyl ethyl ketone are from Ref. 21.

[e] Union Carbide Corporation was merged into Dow Chemical Company in February 2001.

[f] U.S. producer data for methyl isobutyl ketone are from Ref. 22.

[g] For cyclohexanone, only major U.S. producers are listed.

Table 5. **Toxicity of Common Ketones**[a]

| | | Toxicological information[b] | | | | | | Exposure limits | |
|---|---|---|---|---|---|---|---|---|---|
| Common name | CAS Registry number | Oral ingestion LD$_{50}$ rat,[c] mg/kg | Inhalation, TC$_{Lo}$ human,[d] ppm | Inhalation, LC$_{Lo}$ rat, ppm/4 h[e] | Skin penetration, LD$_{50}$ rabbit, mg/kg[f] | Eye irritation, human,[g] ppm/ 15 min | Eye injury, rabbit, severe,[h] mg | OSHA PEL, TWA,[i] ppm | OSHA PEL, STEL,[j] ppm |
| | | | | *Aliphatic ketones* | | | | | |
| acetone | [67-64-1] | 5800; TDLo human: 2857 | 500 EYE | 50100 mg/m3/8 h (LC50) | 20000 | 500 ppm | 3.95 | 750 | 1000 |
| methyl ethyl ketone | [78-93-3] | 2737 | | 23500 mg/m3/8 h (LC50) | 6480 | 350 ppm | 80 | 200 | 300 |
| methyl propyl ketone | [107-87-9] | 1600 | 1500 | 2000 | 6500 | | | 200 | 250 |
| methyl isopropyl ketone | [563-80-4] | 148 | | 5700 | 6350 | | 100 mg/24 h MLD | 200 | |
| diethyl ketone | [96-22-0] | 2140 | | 8000 | 20000 | | 50 MLD | 200 | |
| methyl butyl ketone | [591-78-6] | 2590 | 1000 | 8000 (LC50) | 4800 | | 100 open | 5 | |
| methyl isobutyl ketone | [108-10-1] | 2080 | | 23300 mg/m3 (LC50) | 500 mg/24 h MLD | 40 | | 50 | 75 |
| methyl tert-butyl ketone | [75-97-8] | 610 | | | | | | | |
| ethyl propyl ketone | [589-38-8] | 3360 | | 4000 | 3170 | | 500 mg/24 h MLD | | |
| diacetone alcohol | [123-42-2] | 4000 | 100 | | 13500 | 100 | 5 | 50 | |
| methyl amyl ketone | [110-43-0] | 1670[j]j | | 4000 | 12600 | | | 100 | |
| methyl isoamyl ketone | [110-12-3] | 3200 | | 4000 | | | | 50 | |
| ethyl butyl ketone | [106-35-4] | 2760 | | 2000 | 500 open MLD | | 100 MLD | 50 | |
| dipropyl ketone | [123-19-3] | 3730 | | 4000 | 5660 | | 500 mg/24 h MLD | 50 | |
| diisopropyl ketone | [565-80-0] | 3536 | | | | | | | |
| methyl hexyl ketone | [111-13-7] | 3824 (mouse) | | | 500 mg/24 h MLD | | | | |
| ethyl amyl ketone | [106-68-3] | | | | 500 mg/24 h MLD | | | 25 | |
| diisobutyl ketone | [108-83-8] | 5750 | 50 | 2000 | 16000 | 25 MLD | 500 | 25 | |
| | | | | *Unsaturated ketones* | | | | | |
| methyl vinyl ketone | [78-94-4] | 31 | | 7 mg/m3/4 h (LC50) | | | | | |
| methyl isopropenyl ketone | [814-78-8] | 180 | | 125 | 230 | | 0.05 open | | |

Table 5 (*Continued*)

| Common name | CAS Registry Number | Toxicological information[b] | | | | | | Exposure limits | |
|---|---|---|---|---|---|---|---|---|---|
| | | Oral ingestion LD50 rat,[c] mg/kg | Inhalation, TCLo human,[d] ppm | Inhalation, LCLo rat, ppm/4 h[e] | Skin penetration, LD50 rabbit, mg/kg[f] | Eye irritation, human,[g] ppm/15 min | Eye injury, rabbit, severe,[h] mg | OSHA PEL, TWA,[i] ppm | OSHA PEL, STEL,[j] ppm |
| mesityl oxide | [141-79-7] | 1000 | 25 EYE | 9000<br>mg/m3/4 h<br>(LC50) | 5150 | 25 | 4.325 | 15 | 25 |
| isophorone | [78-59-1] | 1870 | 25 | 1840 | 1500[j]j | 25 | 0.92 | 4 | |
| | | | | *Cyclic ketones* | | | | | |
| cyclopentanone | [120-92-3] | | | | 500 mg/24 h | | 100 | | |
| cyclohexanone | [108-94-1] | 1535 | 75 | 8000 (LC50) | 948 | 75 ppm | 4.74 | 25 | |
| | | | | *Aromatic ketones* | | | | | |
| acetophenone | [98-86-2] | 815 | | | 10 mg/24 h open | | 0.771 | | |
| propiophenone | [93-55-0] | 4490 | | | 4490 | | 500 mg/24 h<br>MLD | | |
| benzophenone | [119-61-9] | 2895 (mouse) | | | | | | | |
| | | | | *Diketones* | | | | | |
| 2,3-butanedione | [431-03-8] | 250 (mouse);<br>human: 720 | | | 500 mg/24 h<br>MOD | | | | |
| 2,3-pentanedione | [600-14-6] | 3000 | | | 500 mg/24 h<br>MOD | | | | |
| 2,4-pentanedione | [123-54-6] | 55 | | 1000 | 10 mg/24 h | | 20 | | |
| 2,5-hexanedione | [110-13-4] | 2076 | | 2000 | 6422<br>(Guinea pig) | | 19 | | |
| diphenylethanedione | [134-81-6] | >3000 (mouse) | | | | | 100 mg/24 h | | |

[a] Data are obtained from Ref. 3 unless otherwise noted (see note j).

[b] Exposure dose/concentration: TDLo = lowest dose to cause toxic effects, TCLo = lowest concentration to cause toxic effects, LDLo = lowest dose to cause death, LD50 = dose to cause 50% death, LCLo = lowest concentration to cause death, LC50 = concentration to cause 50% death.

[c] LD50 on rat unless otherwise noted with the effect level and/or tested species. If human was tested, the dose is also given in addition to that on rat or other animals.

[d] Toxic effects on more than eyes unless marked by EYE for eye effects only.

[e] LCLo in ppm with 4-h exposure unless otherwise noted.

[f] LD50 on rabbit in mg/kg unless otherwise noted. Nonlethal dose: MLD = mild toxic effect, MOD = moderate toxic effect.

[g] Eye irritation in 15-min exposure unless no exposure time reported (in ppm only); MLD = mild irritation.

[h] Severe eye injury unless otherwise noted: MLD = mild.

[i] OSHA = Occupational Safety and Health Act of 1970, Section 6; PEL = permissible exposure level in OSHA Air Contaminant Standards (1989); TWA = 8-h time weighted average; STEL = short-term exposure limit.

[j] Ref. 24.

Table 6. **Flammability and Stability of Common Ketones**

| | | Flammability parameters[a] | | | | Stability and reactivity[b] | | |
|---|---|---|---|---|---|---|---|---|
| Common name | CAS Registry Number | Flash point, closed cup, °C | Flammability limit, vol% | | Autoignition temp., °C | Potential hazardous energy sources | Incompatible materials[c] | Hazardous polymerization |
| | | | Lower | Upper | | | | |
| | | | *Aliphatic ketones* | | | | | |
| acetone | [67-64-1] | −18 | 2.6 | 12.8 | 465 | excessive heat, open flame, ignition sources[d] | B, O, R | will not occur |
| methyl ethyl ketone | [78-93-3] | −6.1 | 1.8 | 10.0 | 516 | | B, O, SR | will not occur[d] |
| methyl propyl ketone | [107-87-9] | 6.9 | 1.5 | 8.2 | 452 | | SB, O, R | will not occur |
| methyl isopropyl ketone | [563-80-4] | 6.0 | 1.8 | 9.0 | 475 | | SB, SO, SR | |
| diethyl ketone | [96-22-0] | 13 | 1.5 | 8.0 | 452 | | SB, O, R | |
| methyl butyl ketone | [591-78-6] | 23 | 1.2 | 8.0 | 423 | | SB, O, R | |
| methyl isobutyl ketone | [108-10-1] | 13 | 1.2 | 8.0 | 448 | | SB, O | will not occur |
| methyl *sec*-butyl ketone | [565-61-7] | 12 | 1.3 | 7.8 | 447 | | SB, O, R | |
| methyl *tert*-butyl ketone | [75-97-8] | 12 | 1.3 | 7.3 | 461 | | SO | |
| ethyl propyl ketone | [589-38-8] | 14 | 1.3 | 7.7 | 439 | | SB, O, R | |
| diacetone alcohol | [123-42-2] | 58 | 1.8 | 6.9 | 603 | excessive temp. w. base or acid[d] | SB, O, R | will not occur[d] |
| methyl amyl ketone | [110-43-0] | 39 | 1.1 | 7.9 | 393 | | SB, SO, SR | will not occur[d] |
| methyl isoamyl ketone | [110-12-3] | 36 | 1.0 | 8.2 | 191 | | SB, SO, SR | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| ethyl butyl ketone | [106-35-4] | 37 | 1.1 | 7.3 | 410 | | SB, SO, SR | |
| dipropyl ketone | [123-19-3] | 48 | 1.1 | 6.8 | 415 | | SB, SO, SR | |
| diisopropyl ketone | [565-80-0] | 15 | 1.1 | 7.0 | 439 | | SB, O, R | |
| methyl hexyl ketone | [111-13-7] | 51 | 1.0 | 6.1 | 380 | | SB, SO, SR | |
| ethyl amyl ketone | [106-68-3] | 51[e] | | | | | SB, SO, SR | |
| diisobutyl ketone | [108-83-8] | 49 | 0.8 | 6.2 | 396 | | SB, SO, SR | will not occur[d] |
| isobutyl heptyl ketone | [123-18-2] | 85[d] | | | | | SO, B, A[d] | will not occur[d] |
| *Unsaturated Ketones* | | | | | | | | |
| methyl vinyl ketone | [78-94-4] | −6.7[e] | 15.6[e] | 2.1[e] | | heat, light | SB, SO, SR | autopolymerization may occur |
| methyl isopropenyl ketone | [814-78-8] | 21 | 1.8 | 9.0 | | | | |
| mesityl oxide | [141-79-7] | 28 | 1.3 | 8.8 | 345 | heat, flame, ignition sources[d] | SO, B, A | will not occur[d] |
| phorone | [504-20-1] | 79[e] | | | | | SO | |
| isophorone | [78-59-1] | 84 | 0.8 | 3.8 | 460 | | SO, SB, SA | will not occur[d] |
| *Cyclic ketones* | | | | | | | | |
| cyclopentanone | [120-92-3] | 26 | 1.5 | 10.4 | | | SB, SO, SR | will not occur |
| cyclohexanone | [108-94-1] | 44 | 1.1 | 9.4 | 419 | | O, plastics | will not occur |
| cycloheptanone | [502-42-1] | 57[e] | | | | | SB, SO, R | |
| *Aromatic ketones* | | | | | | | | |
| acetophenone | [98-86-2] | 82 | 1.1 | 6.7 | 570 | | SB, SO, SR | |
| propiophenone | [93-55-0] | 99[e] | | | | | SB, SO | |
| phenylacetone | [103-79-7] | 90[e] | | | | heat, sparks, open flame | | will not occur |
| benzophenone | [119-61-9] | 146 | 0.7 | 5.4 | | | SO, SR | will not occur |
| *Diketones* | | | | | | | | |
| 2,3-butanedione | [431-03-8] | 27[f] | | 284[e] | | | SB, O, R, metals | |
| 2,3-pentanedione | [600-14-6] | 19[e] | | | | | SB, O, R | |

Table 6 (*Continued*)

| | | Flammability parameters[a] | | | | Stability and reactivity[b] | | |
|---|---|---|---|---|---|---|---|---|
| Common name | CAS Registry Number | Flash point, closed cup, °C | Flammability limit, vol% | | Autoignition temp., °C | Potential hazardous energy sources | Incompatible materials[c] | Hazardous polymerization |
| | | | Lower | Upper | | | | |
| 2,4-pentanedione | [123-54-6] | 34 | 2.4 | 11.6 | 340 | | SB, SO, R | will not occur |
| 2,5-hexanedione | [110-13-4] | 80[e] | | | 501[f] | | SB, SO, SR | |
| diphenylethanedione | [134-81-6] | 180[e] | | | | | SO | |

[a] Flammability parameters are obtained from Ref. 2 unless otherwise noted (see notes *d–f*).

[b] Stability and reactivity are obtained from Ref. 26 unless otherwise noted (see note *d*).

[c] Abbreviations: A = acid, B = base, O = oxidizing agent, R = reducing agent, S = strong.

[d] Ref. 6.

[e] Ref. 26.

[f] Ref. 3.

Table 7. **U.S. Environmental Regulations on Industrial Ketones**

| Common name | CAS Registry number | CAA VOC (EPA)[a] | CAA HAP[b] | SARA 313[c] | CWA Priority pollutant[d] | RCRA Waste[e] | TSCA Inventory[f] |
|---|---|---|---|---|---|---|---|
| *Aliphatic ketones* | | | | | | | |
| acetone | [67-64-1] | | | | | yes | yes |
| methyl ethyl ketone | [78-93-3] | yes | yes | yes | | yes | yes |
| methyl isopropyl ketone | [563-80-4] | yes | | | | | yes |
| diethyl ketone | [96-22-0] | yes | | | | | yes |
| methyl isobutyl ketone | [108-10-1] | yes | yes | yes | | yes | yes |
| diacetone alcohol | [123-42-2] | yes | | | | | yes |
| methyl amyl ketone | [110-43-0] | yes | | | | | yes |
| methyl isoamyl ketone | [110-12-3] | yes | | | | | yes |
| diisobutyl ketone | [108-83-8] | yes | | | | | yes |
| isobutyl heptyl ketone | [123-18-2] | yes | | | | | yes |
| *Unsaturated ketones* | | | | | | | |
| methyl vinyl ketone | [78-94-4] | yes | | | | | yes |
| methyl isopropenyl ketone | [814-78-8] | yes | | | | | yes |
| mesityl oxide | [141-79-7] | yes | | | | | yes |
| isophorone | [78-59-1] | yes | yes | | yes | | yes |
| Cyclic ketones | | | | | | | |
| cyclohexanone | [108-94-1] | yes | | | | yes | yes |
| *Aromatic ketones* | | | | | | | |
| acetophenone | [98-86-2] | yes | yes | yes | | yes | yes |
| propiophenone | [93-55-0] | yes | | | | | yes |
| benzophenone | [119-61-9] | yes | | | | | yes |
| *Diketones* | | | | | | | |
| 2,3-butanedione | [431-03-8] | yes | | | | | yes |
| 2,4-pentanedione | [123-54-6] | yes | | | | | yes |
| diphenylethanedione | [134-81-6] | yes | | | | | yes |

[a] Ref. 27; VOC here refers to EPAs definition.
[b] Ref. 28.
[c] Ref. 29.
[d] Ref. 30.
[e] Ref. 31.
[f] Ref. 3.

Table 8. **Properties of Cyclic Ketones,**[a]

| CAS name | CAS Registry number | Formula x=n | Boiling point,[b] °C | Melting point, °C | Refractive index, $n^{20}_{D}$ | Density at 20°C,[c] g/L | C=O stretching frequency, max, $cm^{-1}$ | Enol, % |
|---|---|---|---|---|---|---|---|---|
| cyclopropanone | [5009-27-8] | 2 | [d] | | | | | |
| cyclobutanone | [1191-95-3] | 3 | 100–102 | | 1.4195 | 938 | 1788 | 0.55 |
| cyclopentanone | [120-92-3] | 4 | 130 | | 1.4359 | 951 | 1746 | 0.09 |
| cyclohexanone | [108-94-1] | 5 | 156.7 | −47 | 1.4507 | 948 | | |
| cycloheptanone | [502-42-1] | 6 | 179–181 | | 1.4611 | 951 | 1703 | 0.56 |
| cyclooctanone | [502-49-8] | 7 | 74 (1.6) | 42 | | 958 | 1703 | 9.3 |
| cyclononanone | [3350-30-9] | 8 | 93–95 (1.6) | 34 | 1.4770 | 959 | 1702 | 4.0 |
| cyclodecanone | [1502-06-3] | 9 | 107 (1.7) | 29 | 1.4820 | 958 | | 6.1 |
| cycloundecanone | [878-13-7] | 10 | 108 (1.6) | 10 | 1.4804 | | | |
| cyclododecanone | [830-13-7] | 11 | 125 (1.6) | 61 | | 906 | | |
| cyclotridecanone | [832-10-0] | 12 | 138 (1.6) | 32 | 1.4790 | 927 | | |
| cyclotetradecanone | [3603-99-4] | 13 | 155 (1.6) | 53 | | | | |
| cyclopentadecanone | [502-72-7] | 14 | 120 (0.04) | 63 | | 897 | | |
| cyclohexadecanone | [2550-52-9] | 15 | 138 (0.04) | 60 | | | | |
| cycloheptadecanone | [3661-77-6] | 16 | 141 (0.13) | 63 | | | | |
| cyclooctadecanone | [6907-37-5] | 17 | 158 (160) | 72 | | | | |
| cyclononadecanone | [6907-38-6] | 18 | 160 (0.04) | 72 | | | | |
| cyclocosanone | [6907-39-7] | 19 | 171 (0.04) | 59 | | | | |

[a] Refs. 209–212.

[b] At 101.3 kPa (1 atm) unless otherwise indicated in kPa in parentheses.

[c] For solids, the density is given for the liquid at the melting point temperature.

[d] Rapidly polymerizes at room temperature. A stable hydrate, mp 71–72°C, is formed in water.

Table 9. **Physical Properties of 1,2-Diketones**[a]

| CAS name | CAS Registry Number | Synonyms | Boiling point,[b] °C | Melting point, °C | Refractive index, $n^t_D$ | Density, g/L,$d^t_4$ | Color | uv Spectra, $\lambda_{max}$, nm |
|---|---|---|---|---|---|---|---|---|
| *Aliphatic* | | | | | | | | |
| 2,3-pentanedione | [600-14-6] | acetylpropionyl | 108 | -52 | $1.4014^{19}$ | $956.5^{19}$ | yellow | 419 |
| 2,3-hexanedione | [3848-24-6] | acetylbutyryl | 128 | | $1.4130^{20}$ | $934.0^{19}$ | | |
| 3,4-hexanedione | [4437-51-8] | bipropionyl | 130 | | $1.4100^{20}$ | $941.0^{21}$ | | 435 |
| 4-methyl-2,3-pentanedione | [7493-58-5] | acetylisobutyrl | 115–116 | | | $921.5^{11}$ | yellow | 429 |
| 3,4-heptanedione | [13706-89-3] | propionylbutyrl | 147 (98) | | | $885.0^{0}$ | | |
| 5-methyl-2,3-hexanedione | [13706-86-0] | acetylisovaleryl | 138 | | $1.4119^{20}$ | $908.0^{22}$ | | 432 |
| 2,3-octanedione | [585-25-1] | acetylcaproyl | 172–173 (98) | | | | | |
| 4,5-octanedione | [5455-24-3] | bibutyryl | 168 | | | $934.0^{0}$ | yellow | 435 |
| 2,5-dimethyl-3,4-heptanedione | [4388-87-8] | biisobutyryl | 144–145 | | $1.4206^{20}$ | $923.2^{20}$ | | 436 |
| 5-methyl-3,4-heptanedione | [13678-56-3] | | 63–67 (5.3) | | | | | |
| 6-methyl-3,4-heptanedione | [3131-90-6] | | 53–54 (2.0) | | $1.4151^{20}$ | $901.9^{20}$ | | |
| *Cyclic* | | | | | | | | |
| 1,2-cyclopentanedione | [3008-40-0] | | 105 (2.7) | 55–56 | | | | |
| 1,2-cyclohexanedione | [765-87-7] | | 193–195 | 35–38 | $1.4995^{20}$ | | | |
| *Aromatic* | | | | | | | | |
| benzil | [134-81-6] | bibenzoyl | 346–348<br>188 (1.6) | 94–95 | | | yellow | |
| 1-phenyl-1,2-propanedione | [579-07-7] | acetylbenzoyl | 125 (3.1) | | | $1101^{20}$ | | |
| 1,2-naphthalendione | [524-42-5] | 1,2-naphtho-quinone | | 145–147 (dec) | | | golden yellow | |

[a] Refs. 209, 224–226.

[b] At 101.3 kPa (1 atm) unless otherwise indicated in kPa in parentheses.

Table 10. **Physical Properties of 1,3-Diketones**[a]

| CAS name | CAS Registry number | Synonyms | Boiling point,[b] °C | Melting point, °C | Density, g/L |
|---|---|---|---|---|---|
| | | *Aliphatic* | | | |
| 2,4-hexanedione | [3002-24-2] | propionylacetone | 158 | | 959 |
| 3,5-heptanedione | [7424-54-6] | dipropionylmethane | 47 (0.8) | | 944.5 |
| 2,4-heptanedione | [7307-02-0] | butyrylacetone | 174–175 | | 941.1[c] |
| 3,5-octanedione | [6320-18-9] | butyrylpropionyl-methane | 189–190 | | |
| 5-methyl-2,4-hexanedione | [7307-03-1] | isobutyrylacetone | 168 | | |
| 2,6-dimethyl-3,5-heptanedione | [18362-64-6] | diisopropionylmethane | 66 (1.1) | | |
| 2,4-octanedione[d] | [14090-87-0] | valerylacetone | 79–83 (2.7) | | 923.3 |
| 5,5-dimethyl-2,4-hexanedione | [29284-62-6] | pivaloylacetone | 164–167 (99) | | |
| 6-methyl-2,4-heptanedione | [3002-23-1] | isovalerylacetone | 73 (2.4) | | |
| | | *Cyclic* | | | |
| 1,3-cyclopenta nedione | [3859-41-4] | | | 151–153 | |
| 1,3-cyclohexa nedione | [504-02-9] | dihydroresorcinol | | 103–105 | |
| 5,5-dimethyl-1,3-cyclohexa nedione | [126-81-8] | dimedone, methone | | 149–151 | |
| | | *Aromatic* | | | |
| 1-phenyl-1,3-butanedione | [93-91-4] | benzoylacetone | 98–100 (0.3) | 58–60 | 1090 |
| 1-phenyl-1,3-pentanedione | [5331-64-6] | benzoylpropionylmethane | 92–94 (0.13) | | |
| 1,3-diphenyl-1,3-propanedione | [120-46-7] | dibenzoylmethane | 219–221 | 77.5–79 | |
| 1-phenyl-2,4-pentanedione[e] | [3318-61-4] | | 144 | | |

[a] Refs. 209, 224, 244, and 245.

[b] At 101.3 kPa (1 atm) unless otherwise indicated in kPa in parentheses.

[c] At 15°C.

[d] $n^{20}_{D}=1.4559$.

[e] $n^{20}_{D}=1.5837$.

Table 11. **Enol and Chelating Properties of 1,3-Diketones**

| | | | Copper chelate | |
|---|---|---|---|---|
| 1,3-Diketone | Enol, % | Refractive index, $n^{t}_{D}$ | Color | Melting point, °C |
| *Aliphatic* | | | | |
| 2,4-pentanedione | 76.4 | | | |
| 2,4-hexanedione | 80.2 | 1.4516 $^{20}$ | green | 198 |
| 3,5-heptanedione | | | | 209–214 |
| 2,4-heptanedione | 83.6 | | blue | 161 |
| 3,5-octanedione | | | blue | 158 |
| 5-methyl-2,4-hexanedione | | | | 171 |
| *Cyclic* | | | | |
| 1,3-cyclohexane-dione | 100 | | | |
| *Aromatic* | | | | |
| 1-phenyl-1,3-butanedione | 99 | | sea green | 199 |
| 1-phenyl-1,3-pentanedione | | 1.5731 $^{25}$ | sea green | 135 |
| 1,3-diphenyl-1,3-propanedione | | | green | 296–300 |

Table 12. **Physical Properties of 1,4-Diketones**[a]

| CAS name | CAS Registry number | Common name | Boiling point,[b], °C | Melting point, °C | Refractive index, $n^{20}_{D}$ |
|---|---|---|---|---|---|
| 3,4-dimethyl-2,5-hexanedione | [25234-79-1] | | 92 (4.0) | | 1.4330 |
| 3,3,4,4-tetramethyl-2,5-hexanedione | [23328-38-3] | | 40 (0.7) | | 1.4522 |
| 2,5-heptanedione | [1703-51-1] | acetylpropionylethane | 90 (2.8) | | |
| 3,6-octanedione | [2955-65-9] | dipropionylethane | 98 (1.9) | 34–35 | |
| 6-methyl-2,5-heptanedione | [13901-85-4] | | 91 (1.6) | | |
| 2,5-decanedione | [41368-32-5] | | 132 (2.3) | | |
| 2,5-dodecanedione | [32781-66-1] | | 148 (1.6) | 40.5 | |
| 1,4-cyclohexanedione | [637-88-7] | | | 77–78.5 | |
| 1,4-diphenyl-1,4-butanedione | [495-71-6] | 1,2-dibenzoylethane | | 145–147 | |

[a] Refs. 224 and 265.

[b] At pressure in kPa in parentheses; to convert kPa to mm Hg, multiply by 7.5.