

Intermediates



# 1,3-Dioxolane



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# BASF – The Chemical Company

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**BASF is the world's leading chemical company: The Chemical Company. Its portfolio ranges from chemicals, plastics, performance products and crop protection products to oil and gas. We combine economic success, social responsibility and environmental protection. Through science and innovation we enable our customers in almost all industries to meet the current and future needs of society. Our products and system solutions contribute to conserving resources, ensuring healthy food and nutrition and helping to improve the quality of life. We have summed up this contribution in our corporate purpose: We create chemistry for a sustainable future.**

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## Top intermediates supplier

The BASF Group's Intermediates division develops, produces and markets a comprehensive portfolio of more than 600 intermediates around the world. The most important of the division's product groups include amines, diols, polyalcohols, acids and specialties. Among other applications, intermediates are used as starting materials for coatings, plastics, pharmaceuticals, textile fibers, detergents and crop protectants. Innovative intermediates from BASF help to improve the properties of final products and the efficiency of production processes. The ISO 9001:2000-certified Intermediates division operates plants at production sites in Europe, Asia and the Americas.



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## 1,3-Dioxolane a powerful aprotic solvent

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1,3-Dioxolane is a powerful aprotic solvent for use in formulations, in production processes or even as a reactant itself. Dioxolane has a very good toxicity profile.

Many applications of dioxolane are due to its ability to rapidly dissolve polar polymers, such as polyesters, epoxies and urethanes. Its small size allows it to rapidly penetrate the polymer, resulting in rapid application rates for various coating processes. Its low boiling point helps achieve high throughput or fast drying.

Dioxolane is also an essential ingredient in important industrial polymers and certain niche pharmaceutical intermediates.

Whether as a solvent or reagent, whether for new or existing applications, BASF dioxolane meets rigid standards set for industries that cannot tolerate impurities. The physical, chemical and applications information contained in this brochure can help you decide whether BASF's high-purity grade of dioxolane meets your requirements.

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# Applications as solvent

Dioxolane is increasingly used in the formulation of water-borne coatings. While a VOC itself, dioxolane can maximize the amount of solids and water due to its high solvency and water solubility.

With its strong solvency and favorable toxicity profile, dioxolane is rapidly finding acceptance as a replacement for halogenated, aromatic, and problematic solvents such as methyl ethyl ketone.

## Physical property comparisons

	Diethyl ether	Methylene chloride	Tetrahydrofuran	1,1,1-Trichloroethane	1,3-Dioxolane	Methyl ethyl ketone	Ethylene dichloride	1,4-Dioxane	Toluene
MW [g/mol]	74.1	84.9	72.1	133	74.1	72.1	99	88.1	92.1
BP [C]	34.5	39.67	65.98	74.07	76.35	79.51	83.57	101.3	110.7
Vapor pressure [hPa] (20C)	585.2	475.67	171.7	131.95	107.16	95.08	82.59	37.88	29.22
Freezing point [C]	-116.3	-95.14	-108.5	-30.05	-95	-86.67	-35.66	11.8	-94.97
Flash point [C]	-40	None	0.48	None	-5	-6	13	11	6
Density [g/ml] (20C)	0.71	1.33	0.89	1.34	1.06	0.8	1.25	1.03	0.87
Viscosity [mPa·s] (25C)	0.23	0.41	0.48	0.77	0.59	0.39	0.78	1.19	0.55
Dielectric constant	4	8.9	7.5	7.58	7.13	18.5	10.4	2.2	2.38
Dipole moment (Debye)	1.15	1.6	1.63	1.87	1.5	3.3	1.8	0.4	0.4
Specific heat [J/g·K]	2.34	1.19	1.7	1.08	1.64	2.19	1.3	1.74	1.69
Heat of vapor [J/g]	367.26	344.57	444.51	243.68	502	481.43	358.52	455.48	412.89
Evap. rate (n-butyl acetate = 1)	11.8	14.5	8	6.0	3.5	3.8	5.1	2.2	1.9
Solubility, H <sub>2</sub> O in, %	1.3	0.14	100	0.04	100	27.3	0.18	100	0.05
Solubility, in H <sub>2</sub> O, %	6.5	1.32	100	0.13	100	12.1	0.95	100	0.05
Solubility parameter, (J/cm <sup>3</sup> ) <sup>1/2</sup>	15.4	20.37	18.97	17.25	42.74	18.88	20.26	20.54	18.25
Hydrogen bonding group	M	P	M	P	M	M	P	M	P



### Solubility of polymers in dioxolane

Polar polymers are susceptible to softening or dissolving in dioxolane. Traditionally, chlorinated solvents were used extensively for materials such as polycarbonates, acrylates, cellulose, urethanes, phenolics, nitriles, urea formaldehydes, alkyds, etc. However, dioxolane is finding increasing use with these and other polymer systems such as polyesters, vinyls, epoxies and halogen-containing polymers.

A dye solution containing an acrylate copolymer and an alkyd can be held together with dioxolane to form a tight bonding film to polyester and acrylates. Solutions for casting films of cyanoethylated carbohydrates are prepared in dioxolane.

A phenoxy resin can be prepared in a special quaternary ammonium or phosphonium salt solution containing dioxolane. Urea and phenol-formaldehyde resins have extended pot life when prepared in dioxolane.

Dioxolane can be used as a seaming solvent to apply polyester labels to small and large plastic bottles containing soft-drinks, water, or other liquids. A bead of dioxolane is applied continuously to the polyester film, which is quickly folded over the bead and bonds. The dioxolane quickly softens the surface, and the polymer chains intertwine and bond. Dioxolane is also used to bond acrylic polymers to themselves.

Dioxolane is the material of choice for plasticizing polyacrylamide so that the material can be formed into useful objects. PVC will also dissolve in dioxolane.

### Polyester film coating

Polyester film coatings can be applied at greater machine speed using dioxolane as solvent because of its superior penetrating power. Its ability to both solubilize pigments and also rapidly soften polyester films allows dioxolane-based inks to outperform other solvent-based inks. Dioxolane is also fast-drying, further lending itself to high-speed coating and printing operations.

Because of its proclivity for solubilizing polymers, dioxolane can be used in paint, film and photoresist removers. Removal of a crosslinked alkyd resin can be achieved within 30 minutes of applying dioxolane.



# Applications in polymers

## Use of dioxolane as a reactant

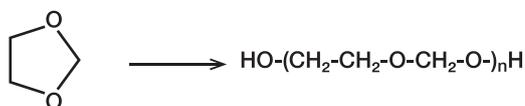
Although dioxolane is well-known as a solvent, or as an inhibitor in 1,1,1-trichloroethane, it is not widely recognized that this molecule undergoes numerous chemical transformations to produce many interesting and useful molecules. Some of these reactions are highly distinctive and specific.

## Homo- and copolymerization with aldehydes

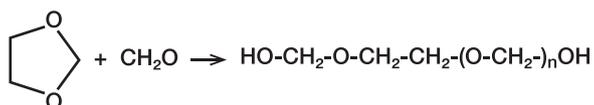
There are many publications on dioxolane's use as a monomer or comonomer in the formation of polyacetals.

Most polymerizations involving dioxolane, either with itself or with aldehydes and ethers, proceed via a cationic mechanism, using strong Lewis acids such as  $\text{BF}_3$ -etherate,  $\text{SbF}_5$ ,  $\text{HClO}_4$ ,  $\text{CF}_3\text{SO}_3\text{H}$ ,  $\text{AsF}_5$ , etc.

### For homopolymerization:



### Used as a comonomer with formaldehyde to produce stable POMs – Polyoxymethylene:



It is also used as a comonomer with formaldehyde homologs such as 1,3,5-trioxane and tetraoxocane. Dioxolane can copolymerize with THF. To prepare polyacetals with improved lubricating properties, dioxolane can be oligomerized with stearaldehyde, then mixed with a high MW trioxane-dioxolane copolymer. Cationically active polydioxolane when mixed with polystyrene will form grafts without any gel.

## Participation in various polymer systems

Dioxolane is used in the photoinitiation of styrene and in the cationically catalyzed copolymerization with styrene. Maleic anhydride is polymerized in the presence of dioxolane to give a viscous oligomer with dioxolane end groups.

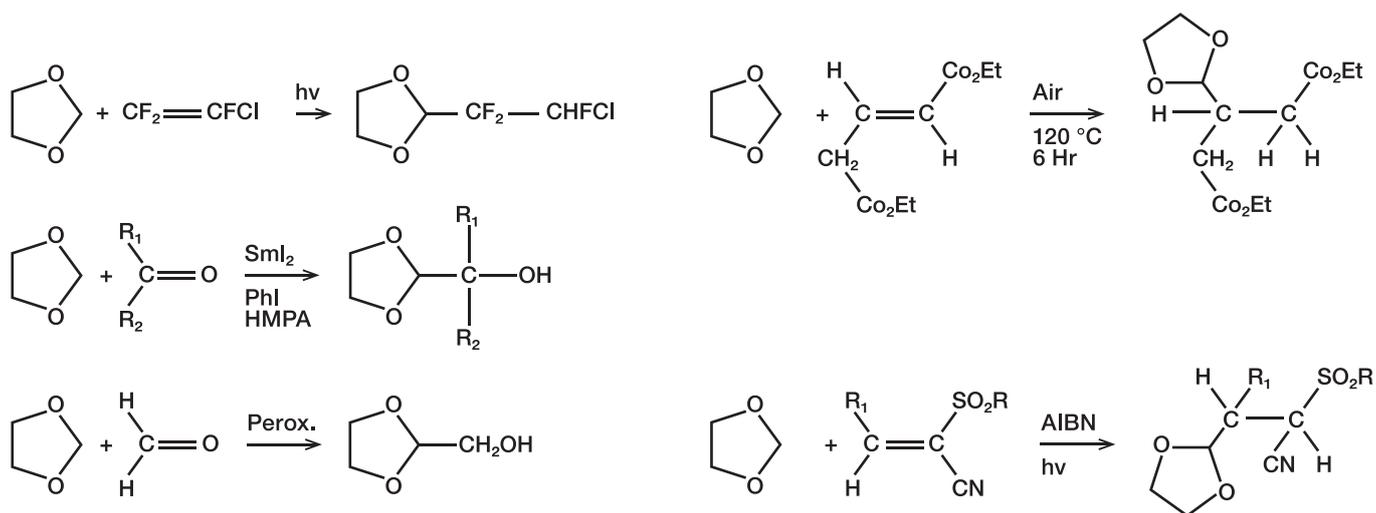
When used as part of the initiation system, dioxolane allows narrow, controlled MW distribution in the production of vinyl ether polymers.

Dioxolane can serve as a MW regulator in the polymerization of vinyl chloride. It can also serve to stabilize crosslinked PVC.

Cellulose ester graft copolymers are prepared by treating cellulose acetate with dioxolane.

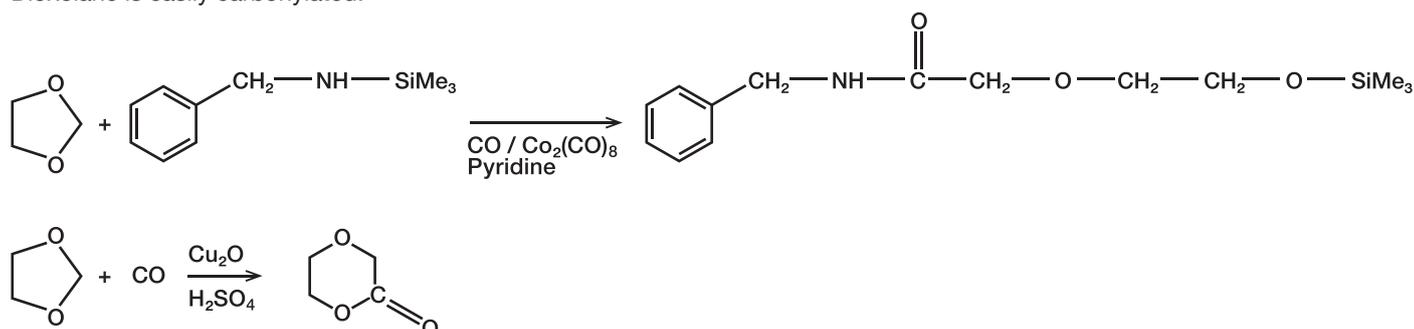
## Doubly activated methylene

The methylene group flanked by two oxygens is susceptible not only to oxidation, but also to radical abstraction of a hydrogen leading to addition elements across a double bond, as the following examples show:



## Carbonylation

Dioxolane is easily carbonylated.



# Special applications

## Organometallic and inorganic systems

Pesticidal compositions containing metal salts of pentachlorophenol and hydroxyl amines can be made in high concentrations with dioxolane, and then diluted with water without precipitating the active ingredients.

Butadiene is cyclotrimerized in the presence of an alkoxytitanium compound and dioxolane. In contrast to failure of a THF-based Grignard reaction on a pentafluoro-aromatic nitrile, replacement of the THF with dioxolane produce the desired compound.

In analogy to most ethylene glycol-based ethers, dioxolane dissolves certain inorganic salts. Dioxolane works well in magnesium perchlorate systems for manufacturing semipermeable membranes.  $\text{LiBH}_4$  is quickly and quantitatively prepared from  $\text{NaBH}_4$  and lithium halide in dioxolane. The formation of clear oil solutions of overbased alkaline earth sulfonates is promoted by dioxolane. Dioxolane serves as part of a solvent package when formulating electrolyte solutions for use in electrical capacitors, for  $\text{WO}_3$  based electrochromic cells, and for an electro-chemical system which causes hydrogen to dissolve in palladium.

Modification of a titanium catalyst with dioxolane will produce alternating copolymers between conjugated diolefins and monoolefins.

## Lithium batteries

The benefits of working with dioxolane when compounding lithium battery electrolyte solutions (organic) have been widely recognized since the early days of lithium systems. BASF's standard technical grade of dioxolane is the highest purity technical grade product available. For demanding lithium battery applications, we also offer a special high-purity grade, with even higher minimum purity of 99.99%, and the lowest water levels available. Lower water grades may require a special shipping container. Please contact a BASF sales representative for further information on very low water grades available in special returnable pressure containers.

## Metal working and electroplating

In this application area, dioxolane functions primarily as a polymer or matrix interaction product. The product obtained by reaction of dioxolane with acetylenic alcohols is useful as a brightening additive in nickel electroplating. Dioxolane allows for surface control in tin-lead electroplating systems. Addition of dioxolane to a mineral acid etching solution increases the effectiveness of the solution. Use of polydioxolane in the electro-deposition of copper produces bright, highly ductile, low stress, good leveling copper deposits.





### Miscellaneous applications

Dioxolane is effective in a number of miscellaneous applications. Dioxolane is an oxygenate for gasoline that effectively increases the octane number. Similarly, dioxolane will increase the cetane number of diesel fuel while raising the pour point and decreasing the gel temperature – which is important for winter driving and diesel storage.

Dioxolane is a solubilizing agent in phenolic resin foams. It is an effective solvent for dissolving and removing tar and asphaltines in the petroleum industry. Dioxolane can be nitrated to form an energetic plasticizer for propellants and explosives. Chlorinated solvents can be stabilized against metal-induced decomposition by use of dioxolane. It can serve as an absorption agent for NOx in a combustion gas scrubber.

Dioxolane is an essential raw material for the production of the anti-viral compound acyclovir.

Dioxolane is finding use in both applying and removing photomasking polymers in silicon wafer printing operations because of its ability to rapidly dissolve these polymers, leaving no residual polymer on the substrates.



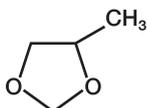
# New developments

BASF technologies are capable of producing other acetals. Sample qualities such as dioxepane, 4-methyl-1,3-dioxolane and glycerol formal are available for evaluation.

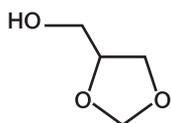
If you need production quantities of any other acetals or further information, please contact one of BASF's technical representatives to discuss your requirements.



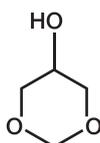
1,3-Dioxepane  
BP: 119C  
CAS No. 505-67-7



4-Methyl-1,3-dioxolane  
BP: 86C  
CAS No. 1072-47-5



Formula Weight: 104.1  
CAS No. 5464-28-8



Formula Weight: 104.1  
CAS No. 4740-78-7

Glycerol Formal  
40:60 mixture  
CAS No. 68442-91-1



# Handling recommendations



## General handling

Since dioxolane is a powerful solvent for many polymers, selecting materials that may contact it in a process can be difficult. Teflon is highly resistant, and substances such as butyl rubber, polyethylene and polypropylene can be used in many applications. Resistance to dioxolane is improved when polymer molecular weight is high or there is a high degree of crosslinking or crystallinity. Specific applications should be tested for polymer swell, softening, degradation and permeability.

Carbon steel can be used for storing and handling pure dioxolane. We recommend storage in an inert atmosphere such as nitrogen to assure product purity for a prolonged period. In this way, both oxygen and atmospheric moisture can be avoided. Contact with acids should be avoided since this will lead to hydrolysis of the dioxolane. Formaldehyde release is usually not a problem since the primary products of hydrolysis are hemiacetals. However, the potential for some formaldehyde release should be kept in mind when designing a process that involves contact with acids.

Never distill dioxolane or any oxygenated solvent to dryness.

## Recovery and recycling

BASF can provide technical information to help customers develop a safe and cost-effective recycling program. In some cases, BASF can also provide final “back-to-specs” purification services, if needed. Please contact a service representative if you need this type of service.

## Peroxides

BASF maintains high purity standards by a number of rigid manufacturing controls. Dioxolane is manufactured in a dry, inert environment and is packaged under nitrogen. This assures product integrity over long periods of storage. Our studies show that peroxide concentration is barely detectable in the ppm range even after storage periods as long as a year.

Peroxides in ethers can decompose to form other impurities. However, unlike ethers such as THF and ethyl ether where peroxides accumulate rapidly, dioxolane peroxides are much more labile and tend not to build to high levels. Safe decomposition of peroxide in dioxolane can be accelerated simply by warming the dioxolane under nitrogen to 65°C for a brief period.

In many instances where dioxolane is used, air exposure cannot be avoided. In these cases, peroxide concentration should be monitored, since peroxides could form undesirable chemical by-products in the system.

With some chemicals there is a tendency for peroxides to become isolated by phase separation, which results in the formation of a high peroxide layer. This phenomenon is unlikely in dioxolane because of the very high solubility of peroxides and other oxygenated organic material in dioxolane.

Peroxide formation is effectively stopped by using a phenolic antioxidant such as BHT. Dioxolane contains 75 ppm BHT unless otherwise specified.

The highest standards of safety, product stewardship and responsible care should be maintained when using and recycling dioxolane.

For safety data, please refer to the material safety data sheets.

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[www.basf.com/performance-materials](http://www.basf.com/performance-materials)

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