

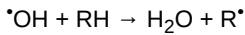
Hydroxyl radical

The **hydroxyl radical**, **OH**, is the neutral form of the hydroxide ion (OH^-). Hydroxyl radicals are highly reactive (easily becoming hydroxyl groups) and consequently short-lived; however, they form an important part of radical chemistry.^[2] Most notably hydroxyl radicals are produced from the decomposition of hydroperoxides (ROOH) or, in atmospheric chemistry, by the reaction of excited atomic oxygen with water. It is also an important radical formed in radiation chemistry, since it leads to the formation of hydrogen peroxide and oxygen, which can enhance corrosion and SCC in coolant systems subjected to radioactive environments. Hydroxyl radicals are also produced during UV-light dissociation of H_2O_2 (suggested in 1879) and likely in Fenton chemistry, where trace amounts of reduced transition metals catalyze peroxide-mediated oxidations of ganic compounds.

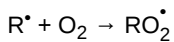
In organic synthesis, hydroxyl radicals are most commonly generated by photolysis of 1-hydroxy-2(1H)-pyridinethione

The hydroxyl radical is often referred to as the "detergent" of the troposphere because it reacts with many pollutants, decomposing them through "cracking", often acting as the first step to their removal. It also has an important role in eliminating some greenhouse gases like methane and ozone.^[3] The rate of reaction with the hydroxyl radical often determines how long many pollutants last in the atmosphere, if they do not undergo photolysis or are rained out. For instance methane, which reacts relatively slowly with hydroxyl radical, has an average lifetime of >5 years and many CFCs have lifetimes of 50 years or more. Other pollutants, such as larger hydrocarbons, can have very short average lifetimes of less than a few hours.

The first reaction with many volatile organic compounds (VOCs) is the removal of a hydrogen atom, forming water and an alkyl radical (R').



The alkyl radical will typically react rapidly with oxygen forming a peroxy radical.



The fate of this radical in the troposphere is dependent on factors such as the amount of sunlight, pollution in the atmosphere and the nature of the alkyl radical that formed it.^[4]

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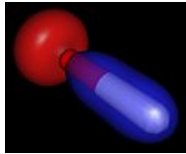
External links

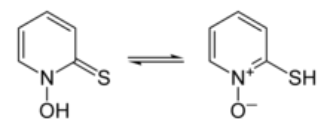
Biological significance

Hydroxyl radicals can occasionally be produced as a byproduct of immune action. Macrophages and microglia most frequently generate this compound when exposed to very specific pathogens, such as certain bacteria. The destructive action of hydroxyl radicals has been implicated in several neurological autoimmune diseases such as HAND when immune cells become over-activated and toxic to neighboring healthy cells.^[5]

The hydroxyl radical can damage virtually all types of macromolecules: carbohydrates, nucleic acids (mutations), lipids (lipid peroxidation), and amino acids (e.g. conversion of Phe to *m*-Tyrosine and *o*-Tyrosine).^[6] The hydroxyl radical has a very short *in vivo* half-life of approximately 10^{-9} seconds and a high reactivity.^[7] This makes it a very dangerous compound to the organism.^{[8][9]}

Unlike superoxide, which can be detoxified by superoxide dismutase, the hydroxyl radical cannot be eliminated by an enzymatic reaction.^[8]

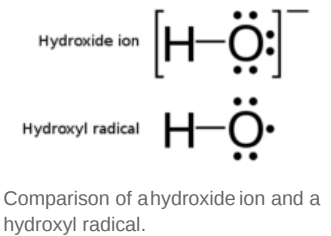
Hydroxyl radical	
 	
Names	
IUPAC name	Hydroxyl radical
Systematic IUPAC name	Oxidanyl ^[1] (substitutive) Hydridoxygen(•) ^[1] (additive)
Other names	Hydroxy Hydroxyl λ ¹ -Oxidanyl
Identifiers	
CAS Number	3352-57-6
3D model (JSmol)	Interactive image
ChEBI	CHEBI:29191
ChemSpider	138477 ✓
Gmelin Reference	105
KEGG	C16844 ✓
PubChem CID	157350
InChI	
SMILES	
Properties	
Chemical formula	HO
Molar mass	17.01 g·mol ^{−1}
Thermochemistry	
Std molar entropy (S [∘] ₂₉₈)	183.71 J K ^{−1} mol ^{−1}
Std enthalpy of formation (Δ _f H [∘] ₂₉₈)	38.99 kJ mol ^{−1}
Except where otherwise noted, data are given for materials in their standard state (at 25 °C [77 °F], 100 kPa).	
Infobox references	



Skeletal formulae of 1-hydroxy-2(1*H*)-pyridinethione and its tautomer

Importance in Earth's atmosphere

The hydroxyl $\cdot\text{OH}$ radical is one of the main chemical species controlling the oxidizing capacity of the global Earth atmosphere. This oxidizing reactive species has a major impact on the concentrations and distribution of greenhouse gases and pollutants in the Earth atmosphere. It is the most widespread oxidizer in the troposphere, the lowest part of the atmosphere. Understanding $\cdot\text{OH}$ variability is important to evaluating human impacts on the atmosphere and climate. The $\cdot\text{OH}$ species has a lifetime in the Earth atmosphere of less than one second.^[10] Understanding the role of $\cdot\text{OH}$ in the oxidation process of methane (CH_4) present in the atmosphere to first carbon monoxide (CO) and then carbon dioxide (CO_2) is important for assessing the residence time of this greenhouse gas, the overall carbon budget of the troposphere, and its influence on the process of global warming. The lifetime of $\cdot\text{OH}$ radicals in the Earth atmosphere is very short, therefore $\cdot\text{OH}$ concentrations in the air are very low and very sensitive techniques are required for its direct detection.^[11] Global average hydroxyl radical concentrations have been measured indirectly by analyzing methyl chloroform (CH_3CCl_3) present in the air. The results obtained by Montzka *et al.* (2011)^[12] shows that the interannual variability in $\cdot\text{OH}$ estimated from CH_3CCl_3 measurements is small, indicating that global $\cdot\text{OH}$ is generally well buffered against perturbations. This small variability is consistent with measurements of methane and other trace gases primarily oxidized by $\cdot\text{OH}$, as well as global photochemical model calculations.



In 2014, researchers reported their discovery of a "hole" or absence of hydroxyl throughout the entire depth of the troposphere across a large region of the tropical West Pacific. They suggested that this hole is permitting large quantities of ozone-degrading chemicals to reach the stratosphere, and that this may be significantly reinforcing ozone depletion in the polar regions with potential consequences for the climate of the Earth.^[13]

Astronomical importance

First detection of interstellar $\cdot\text{OH}$

The first experimental evidence for the presence of 18 cm absorption lines of the hydroxyl ($\cdot\text{OH}$) radical in the radio absorption spectrum of Cassiopeia A was obtained by Weinreb et al. (Nature, Vol. 200, pp. 829, 1963) based on observations made during the period October 15–29, 1963.^[14]

Important subsequent reports of astronomical $\cdot\text{OH}$ detections

Year	Description
1967	$\cdot\text{HO}$ Molecules in the Interstellar Medium Robinson and McGee. One of the first observational reviews of $\cdot\text{OH}$ observations. $\cdot\text{OH}$ had been observed in absorption and emission, but at this time the processes which populate the energy levels are not yet known with certainty, so the article does not give good estimates of $\cdot\text{OH}$ densities. ^[15]
1967	Normal $\cdot\text{HO}$ Emission and Interstellar Dust Clouds Heiles. First detection of normal emission from $\cdot\text{OH}$ in interstellar dust clouds. ^[16]
1971	Interstellar molecules and dense clouds D. M. Rank, C. H. Townes, and W. J. Welch. Review of the epoch about molecular line emission of molecules through dense clouds. ^[17]
1980	$\cdot\text{HO}$ observations of molecular complexes in Orion and β Aurus. Baud and Wouterloot. Map of $\cdot\text{OH}$ emission in molecular complexes Orion and β Aurus. Derived column densities are in good agreement with previous CO results. ^[18]
1981	Emission-absorption observations of $\cdot\text{HO}$ in diffuse interstellar clouds Dickey, Crovisier and Kazès. Observations of fifty eight regions which show $\cdot\text{OH}$ absorption were studied. Typical densities and excitation temperature for diffuse clouds are determined in this article. ^[19]
1981	Magnetic fields in molecular clouds — $\cdot\text{HO}$ Zeeman observations Crutcher, Troland, and Heiles. $\cdot\text{OH}$ Zeeman observations of the absorption lines produced in interstellar dust clouds toward 3C 133, 3C 123, and W51. ^[20]
1981	Detection of interstellar $\cdot\text{HO}$ in the Far-Infrared. J. Storey, D. Watson, C. Townes. Strong absorption lines of $\cdot\text{OH}$ were detected at wavelengths of 119.23 and 119.44 microns in the direction of Sgr B2. ^[21]
1989	Molecular outflows in powerful $\cdot\text{HO}$ megamasers. Baan, Haschick, and Henkel. Observations of $\cdot\text{H}$ and $\cdot\text{OH}$ molecular emission through $\cdot\text{OH}$ megamasers galaxies, in order to get a FIR luminosity and maser activity relation. ^[2]

Energy levels

$\cdot\text{OH}$ is a diatomic molecule. The electronic angular momentum along the molecular axis is +1 or −1, and the electronic spin angular momentum $S = \frac{1}{2}$. Because of the orbit-spin coupling, the spin angular momentum can be oriented in parallel or anti arallel directions to the orbital angular momentum, producing the splitting into $\Pi_{3/2}$ and $\Pi_{1/2}$ states. The $^2\Pi_{3/2}$ ground state of $\cdot\text{OH}$ is split by lambda doubling interaction (an interaction between the nuclei rotation and the unpaired electron motion around its orbit). Hyperfine interaction with the unpaired spin of the proton further splits the levels.

Chemistry of the molecule $\cdot\text{OH}$

In order to study gas phase interstellar chemistry, it is convenient to distinguish two types of interstellar clouds: diffuse clouds, with $T = 30\text{--}100$ K and $n = 10\text{--}1000\text{ cm}^{-3}$, and dense clouds, with $T = 10\text{--}30$ K and density $n = 10^4\text{--}10^3\text{ cm}^{-3}$. Ion chemical routes in both dense and diffuse clouds have been established for some works (Hartquist, *Molecular Astrophysics*, 1990).

$\cdot\text{OH}$ production pathways

The $\cdot\text{OH}$ radical is linked with the production of H_2O in molecular clouds. Studies of $\cdot\text{OH}$ distribution in Taurus Molecular Cloud-1 (TMC-1)^[23] suggest that in dense gas, $\cdot\text{OH}$ is mainly formed by dissociative recombination of H_3O^+ . Dissociative recombination is the reaction in which a molecular ion recombines with an electron and dissociates into neutral fragments. Important formation mechanisms for $\cdot\text{OH}$ are:





•OH destruction pathways

Experimental data on association reactions of $\cdot\text{H}$ and $\cdot\text{OH}$ suggest that radiative association involving atomic and diatomic neutral radicals may be considered as an effective mechanism for the production of small neutral molecules in the interstellar clouds.^[24] The formation of O_2 occurs in the gas phase via the neutral exchange reaction between O and $\cdot\text{OH}$, which is also the main sink for $\cdot\text{OH}$ in dense regions^[23]

We can see that atomic oxygen takes part both in the production and destruction of $\cdot\text{OH}$, so the abundance of $\cdot\text{OH}$ depends mainly on the H_3^+ abundance. Then, important chemical pathways leading from $\cdot\text{OH}$ radicals are:



Rate constants and relative rates for important formation and destruction mechanisms

Rate constants can be derived from the dataset published in a website.^[25] Rate constants have the form:

$$k(T) = \alpha \left(\frac{T}{300}\right)^\beta \times \exp\left(-\frac{\gamma}{T}\right) \text{ cm}^3 \text{ s}^{-1}$$

The following table has the rate constants calculated for a typical temperature in a dense cloud $T = 10 \text{ K}$.

Reaction	$k \text{ (} T = 10 \text{ K) cm}^3 \text{ s}^{-1}$
<u>1a</u>	3.29×10^{-6}
<u>1b</u>	1.41×10^{-7}
<u>2a</u>	4.71×10^{-7}
<u>3a</u>	5.0×10^{-11}
<u>4a</u>	1.26×10^{-6}
<u>5a</u>	2.82×10^{-6}
<u>1A</u>	7.7×10^{-10}
<u>2A</u>	3.5×10^{-11}
<u>3A</u>	1.38×10^{-10}
<u>4A</u>	1.0×10^{-10}
<u>5A</u>	3.33×10^{-14}

Formation rates r_{ix} can be obtained using the rate constants $k(T)$ and the abundances of the reactants species C and D:

$$r_{\text{ix}} = k(T)_{\text{ix}}[\text{C}][\text{D}]$$

where [Y] represents the abundance of the species Y. In this approach, abundances were taken from *The UMIST database for astrochemistry 2006*, and the values are relatives to the H₂ density. Following table shows the ratio r_{ix}/r_{1a} in order to get a view of the most important reactions.

	<i>r</i> _{1a}	<i>r</i> _{1b}	<i>r</i> _{2a}	<i>r</i> _{3a}	<i>r</i> _{4a}	<i>r</i> _{5a}
<i>r</i> _{1a}	1.0	0.043	0.013	0.035	3.6×10^{-5}	0.679

The results suggest that (1a) reaction is the most prominent reaction in dense clouds. It is in concordance with Harju et al. 2000.

The next table shows the results by doing the same procedure for destruction reaction:

	<i>r</i> _{1A}	<i>r</i> _{2A}	<i>r</i> _{3A}	<i>r</i> _{4A}	<i>r</i> _{5A}
<i>r</i> _{1A}	1.0	6.14×10^{-3}	0.152	3.6×10^{-5}	4.29×10^{-3}

Results shows that reaction 1A is the main sink for OH in dense clouds.

Importance of interstellar OH observations

Discoveries of the microwave spectra of a considerable number of molecules prove the existence of rather complex molecules in the interstellar clouds, and provides the possibility study dense clouds, which are obscured by the dust they contain.^[26] The OH molecule has been observed in the interstellar medium since 1963 through its 18-cm transitions.^[27] In the subsequent years OH was observed by its rotational transitions at far infrared wavelengths, mainly in the Orion region. Because each rotational level of OH is split in by lambda doubling, astronomers can observe a wide variety of energy states from the ground state.

OH as a tracer of shock conditions

Very high densities are required to thermalize the rotational transitions of OH,^[28] so it is difficult to detect far-infrared emission lines from a quiescent molecular cloud. Even at H₂ densities of 10⁶ cm⁻³, dust must be optically thick at infrared wavelengths. But the passage of a shock wave through a molecular cloud is precisely the process which can bring the molecular gas out of equilibrium with the dust, making observations of far-infrared emission lines possible. A moderately fast shock may produce a transient raise in the OH abundance relative to hydrogen. So, it is possible that farinfrared emission lines of OH can be a good diagnostic of shock conditions.

In diffuse clouds

Diffuse clouds are of astronomical interest because they play a primary role in the evolution and thermodynamics of ISM. Observation of the abundant atomic hydrogen in 21 cm has shown good signal-to-noise ratio in both emission and absorption. Nevertheless, HI observations have a fundamental difficulty when they are directed at low mass regions of the hydrogen nucleus, as the center part of a diffuse cloud: the thermal width of the hydrogen lines are of the same order as the internal velocities of structures of interest, so cloud components of various temperatures and central velocities are indistinguishable in the spectrum. Molecular line observations in principle do not suffer from this problem. Unlike HI, molecules generally have excitation temperature $T_{\text{ex}} \ll T_{\text{kin}}$, so that emission is very weak even from abundant species. CO and OH are the most easily studied candidate molecules. CO has transitions in a region of the spectrum (wavelength < 3 mm) where there are not strong background continuum sources, but OH has the 18 cm emission, line convenient for absorption observations.^[19] Observation studies provide the most sensitive means of detections of molecules with subthermal excitation, and can give the opacity of the spectral line, which is a central issue to model the molecular region.

Studies based in the kinematic comparison of OH and HI absorption lines from diffuse clouds are useful in determining their physical conditions, specially because heavier elements provide higher velocity resolution.

OH masers

OH masers, a type of astrophysical maser, were the first masers to be discovered in space and have been observed in more environments than any other type of maser

In the Milky Way, OH masers are found in stellar masers (evolved stars), interstellar masers (regions of massive star formation), or in the interface between supernova remnants and molecular material. Interstellar OH masers are often observed from molecular material surrounding ultracompact H II regions (UC H II). But there are masers associated with very young stars that have yet to create UC H II regions.^[29] This class of OH masers appears to form near the edges of very dense material, place where H₂O masers form, and where total densities drop rapidly and UV radiation from young stars can dissociate the H₂O molecules. So, observations of OH masers in these regions, can be an important way to probe the distribution of the important H₂O molecule in interstellar shocks at high spatial resolutions.

Application in water purification

Hydroxyl radicals play a key role in the oxidative destruction of organic pollutant using a series of methodologies collectively known as advanced oxidation processes (AOPs). The destruction of pollutants in AOPs is based on the non-selective reaction of hydroxyl radicals on organic compounds. It is highly effective against a series of pollutants including pesticides, pharmaceutical compounds,dyes, etc.^{[30][31]}

See also

- Hydroxyl ion absorption
- Hydrogen darkening

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