

Hydroxyl radical

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Hydroxyl in chemistry describes a molecule consisting of an oxygen atom and a hydrogen atom joined by a covalent bond. The neutral form is known as a hydroxyl radical and the singly-charged hydroxyl anion is called hydroxide. When its oxygen atom is covalently bonded within a larger molecule, the hydroxyl group either is, or otherwise is part of, a functional group (**HO-** or **-OH**) .

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Hydroxyl group

The term **hydroxyl group** is used to describe the functional group **-OH** when it is a substituent in an organic compound. Organic molecules containing a hydroxyl group, such that the hydroxyl has a negative inductive effect, are known as alcohols (the simplest of which have the formula $C_n H_{2n+1} -OH$).

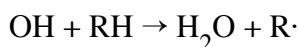
Hydroxyl radical

The hydroxyl radical, OH, is the neutral form of the **hydroxide** ion. **Hydroxyl radicals** are highly reactive and consequently short-lived; however, they form an important part of radical chemistry. Most notably **hydroxyl radicals** are produced from the decomposition of hydro-peroxides (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 H₂O₂ (suggested in 1879) and likely in Fenton chemistry, where trace amounts of reduced transition metals catalyze peroxide-mediated oxidations of organic compounds.

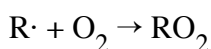
In organic synthesis hydroxyl radicals are most commonly generated by photolysis of *1-Hydroxy-2(1H)-pyridinethione*.

Atmospheric importance

The Hydroxyl radical is often referred to as the "detergent" of the troposphere because it reacts with many pollutants, often acting as the first step to their removal. It also has an important role in eliminating some greenhouse gasses like methane and ozone [1] (<http://www.ipcc.ch/pdf/assessment-report/ar4/wg1/ar4-wg1-chapter2.pdf>). The first reaction with many volatile organic compounds (VOCs) is the removal of a hydrogen atom forming water and an alkyl radical (R·).



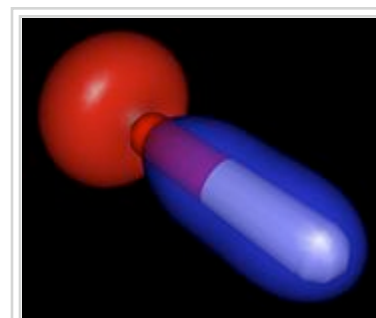
The alkyl radical will typically react rapidly with oxygen forming a peroxy radical.



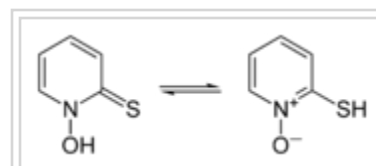
The fate of this radical in the troposphere is dependent on factors such as the amount of sunlight (light from the sun), pollution in the atmosphere and the nature of the alkyl radical that formed it.

Biological significance

The hydroxyl radical has a very short *in vivo* half-life of approx. 10⁻⁹ s and a high reactivity. This makes it a very dangerous compound to the organism. Unlike superoxide, which can be detoxified by superoxide dismutase, the hydroxyl radical cannot be eliminated by an enzymatic reaction, as this would require its diffusion to the enzyme's active site. As diffusion is slower than the half-life of the molecule, it will react with any oxidizable compound in its vicinity. It 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). The only means to protect important cellular structures is the use of antioxidants such as glutathione and of effective repair systems.



Molecular orbital of the hydroxyl radical with unpaired electron



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

Astronomical importance

First detection of interstellar OH

The first experimental evidence for the presence of 18-cm absorption lines of the hydroxyl (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. [[2] (<http://www.nature.com/nature/journal/v201/n4916/abs/201279b0.html>) [link to article]].

Important subsequent report of OH astronomical detections

Year	Description	Reference
1967	<i>OH Molecules in the Interstellar Medium.</i> Robinson and McGee. One of the first observational reviews of OH observations. 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 OH densities.	[3] (http://adsabs.harvard.edu/abs/1967ARA%26A...5..183R)
1967	<i>Normal OH Emission and Interstellar Dust Clouds.</i> Heiles. First detection of normal emission from OH in interstellar dust clouds.	[4] (http://adsabs.harvard.edu/abs/1968ApJ...151..919H)
1971	<i>Interstellar molecules and dense clouds.</i> D. M. Rank, C. H. Townes, and W. J. Welch. Review of the epoch about molecular line emission of molecules through dense clouds.	[5] (http://www.sciencemag.org/cgi/content/refs/174/4014/1083)
1980	<i>OH observations of molecular complexes in Orion and Taurus.</i> Baud and Wouterloot. Map of OH emission in molecular complexes Orion and Taurus. Derived column densities are in good agreement with previous CO results.	[6] (http://adsabs.harvard.edu/abs/1980A%26A....90..297B)
1981	<i>Emission-absorption observations of OH in diffuse interstellar clouds.</i> Dickey, Crovisier and Kazès. Observations of fifty eight regions which show H I absorption were studied. Typical densities and excitation temperature for diffuse clouds are determined in this article.	[7] (http://adsabs.harvard.edu/abs/1981A%26A....98..271D)
1981	<i>Magnetic fields in molecular clouds - OH Zeeman observations.</i> Crutcher, Troland and Heiles. OH Zeeman observations of the absorption lines produced in interstellar dust clouds toward 3C 133, 3C 123, and W51.	[8] (http://adsabs.harvard.edu/abs/1981ApJ...249..134C)

1981	<i>Detection of interstellar OH in the Far-Infrared.</i> J. Storey, D. Watson, C. Townes. Strong absorption lines of OH were detected at wavelengths of 119.23 and 119.44 microns in the direction of Sgr B2.	[9] (http://adsabs.harvard.edu/abs/1981ApJ...244L..27S)
1989	<i>Molecular outflows in powerful OH megamasers.</i> Baan, Haschick and Henkel. Observations of H and OH molecular emission through OH megamasers galaxies, in order to get a FIR luminosity and maser activity relation.	[10] (http://adsabs.harvard.edu/abs/1989ApJ...346..680B)

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 to make studies dense clouds, which are obscured by the dust dust they contain [11] (<http://www.sciencemag.org/cgi/content/refs/174/4014/1083>) (Rank, Townes, and Welch 1971). The OH molecule has been observed in the interstellar medium since 1963 through its 18-cm transitions [12] (<http://www.nature.com/nature/journal/v201/n4916/abs/201279b0.html>) (Weinreb et al. 1963). 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 [13] (<http://adsabs.harvard.edu/abs/1981ApJ...244L..27S>) (Storey, Watson and Townes 1980), 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. An moderately fast shock may produce a transient raise in the OH abundance relative to hydrogen. So, it is possible that far-infrared 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 are directed to low mass regions of the hydrogen nucleus, as the center part of a diffuse cloud: Thermal width of hydrogen lines are the same order as the internal velocities structures of interest, so clouds components of various temperatures and central velocities are indistinguishable in the

spectrum. Molecular lines observations in principle doesn't suffer of this problems. Unlike HI, molecules generally have excitation temperatures $T_{\text{ex}} \ll T_{\text{kin}}$, so that emission is very weak even from abundant species. CO and OH are the most easily studied candidates molecules. CO has transitions in a region of the spectrum (wavelength < 3 mm) where there is not strong background continuum sources, but OH has the 18 cm emission, line convenient for absorption observations (Dickey, Crovisier and Kazès 1980) [14] (<http://adsabs.harvard.edu/abs/1981A%26A....98..271D>) . 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

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 [15] (<http://adsabs.harvard.edu/abs/2003ApJ...593..925A>) (Argon, Reid and Menten 2003). 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 spacial resolutions_.

See also

- Hydroxyl ion absorption
- Hydrogen darkening

Downes, A. and Blunt, T.P. (1879). The effect of sunlight upon hydrogen peroxide. Nature 20, 521.

External links

- Hydroxyl found in atmosphere of Venus (<http://www.physorg.com/news130065276.html>)

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Categories: Hydroxides | Functional groups | Alcohols

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