Hydrogen cyanide

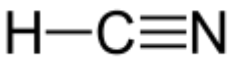
From Wikipedia, the free encyclopedia

Hydrogen cyanide (with the historical common name of **Prussic acid**) is a chemical compound with chemical formula HCN. Hydrogen cyanide is a colorless, extremely poisonous liquid that boils slightly above room temperature at 26 °C (79 °F). Hydrogen cyanide is a linear molecule, with a triple bond between carbon and nitrogen. A minor tautomer of HCN is HNC, hydrogen isocyanide.

Hydrogen cyanide is weakly acidic with a pK_a of 9.2. It partly ionizes in water solution to give the cyanide anion, CN^-. A solution of hydrogen cyanide in water is called hydrocyanic acid. The salts of hydrogen cyanide are known as cyanides.

HCN has a faint, bitter, burnt almond-like odor that some people are unable to detect due to a genetic trait.[2] The volatile compound has been used as inhalation rodenticide and human poison. Cyanide ions interfere with iron-containing respiratory enzymes.

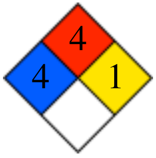
HCN is produced on an industrial scale, and is a highly valuable precursor to many chemical compounds, ranging from polymers to pharmaceuticals.

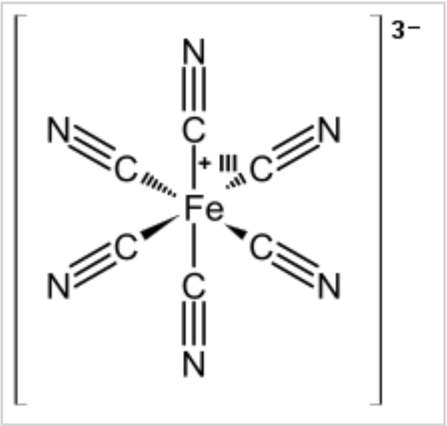
Hydrogen cyanide	
	
IUPAC name formonitrile	
Other names hydrogen cyanide; methanenitrile; hydrocyanic acid; prussic acid; Zyklon B	
Identifiers	
CAS number	74-90-8 ✓
PubChem	768
EC number	200-821-6
UN number	1051 (anhydrous) 1613 (aqueous soln., <20%) 1614 (adsorbed)
RTECS number	MW6825000
SMILES	C#N
Properties	
Molecular formula	HCN
Molar mass	27.0253 g/mol
Appearance	Colorless gas or pale blue highly volatile liquid
Density	0.687 g/cm^3, liquid.
Melting point	−13.4 °C, 260 K, 8 °F
Boiling point	25.6 °C, 299 K, 78 °F
Solubility in water	completely miscible
Acidity (pK_a)	9.21
Refractive index (n_D)	1.2675 [1]
Viscosity	0.201 cP
Structure	
Molecular shape	Linear
Dipole moment	2.98 D
Thermochemistry	
Std enthalpy of formation $\Delta_f H^\circ_{298}$	-4.999 kJ/g
Std enthalpy of combustion $\Delta_c H^\circ_{298}$	-24.6 kJ/g
Specific heat capacity, C	1.328 J/(g·K) (gas) 2.612 J/(g·K) (liquid)

Contents

History of discovery

Hydrogen cyanide was first isolated from a blue dye (Prussian blue) which had been known from 1704 but had a structure which was unknown. It is now known to be a coordination polymer with a complex structure and an empirical formula of hydrated ferric ferrocyanide. In 1752, the French chemist Pierre Macquer made the important step of showing that Prussian blue could be converted to iron oxide plus a volatile component and that these could be used to reconstitute the dye. The new component was what we now know as hydrogen cyanide. Following Macquer's lead, it was first isolated from Prussian blue in pure form and characterized about 1783 by the Swedish chemist Carl Wilhelm Scheele, and was eventually given the German name *Blausäure* (literally "Blue acid") because of its acidic nature in water and its derivation from Prussian blue. In English it became known popularly as *Prussic acid*.

Hazards	
EU Index	006-006-00-X
EU classification	Extremely flammable (**F+**) Very toxic (**T+**) Dangerous for the environment (**N**)
R-phrases	R12, R26, R50/53
S-phrases	(S1/2), S7/9, S16, S36/37, S38, S45, S60, S61
NFPA 704	
Flash point	−17.8 °C (−64 °F)
Autoignition temperature	538 °C
Related compounds	
Related compounds	Cyanogen Cyanogen chloride Trimethylsilyl cyanide Methylidynephosphane
✓ (what is this?) (verify) (http://en.wikipedia.org/w/index.php?title=Hydrogen_cyanide&diff=cur&oldid=267266573) Except where noted otherwise, data are given for materials in their standard state (at 25 °C, 100 kPa)	
Infobox references	



Anion of Prussian blue

In 1787 the French chemist Claude Louis Berthollet showed that Prussic acid did not contain oxygen, an important contribution to acid theory, which had hitherto postulated that acids must contain oxygen[3] (hence the name of oxygen itself, which is derived from Greek elements that mean "acid-former" and are likewise calqued into German as *Sauerstoff*). In 1815 Joseph Louis Gay-Lussac deduced Prussic acid's chemical formula. The radical cyanide in hydrogen cyanide was given its name from the Greek word for blue, again due to its derivation from Prussian blue.

Production and synthesis

Hydrogen cyanide forms in at least limited amounts from many combinations of hydrogen, carbon, and ammonia. Hydrogen cyanide is currently produced in great quantities by several processes, as well as being a recovered waste product from the manufacture of acrylonitrile.[4] In the year 2000, 732,552 tons were produced in the US.[5] The most important process is the Andrussov oxidation invented by Leonid Andrussow at IG Farben in which methane and ammonia react in the presence of oxygen at about 1200 °C over a platinum catalyst:[6]

$$2\ CH_4 + 2\ NH_3 + 3\ O_2 \rightarrow 2\ HCN + 6\ H_2O$$

The energy needed for the reaction is provided by the partial oxidation of methane and ammonia.

Of lesser importance is the Degussa process (BMA process) in which no oxygen is added and the energy must be transferred indirectly through the reactor wall:[7]

$$CH_4 + NH_3 \rightarrow HCN + 3H_2$$

This reaction is akin to steam reforming, the reaction of methane and water to give carbon monoxide and hydrogen.

In the Shawinigan Process, ammonia and natural gas are passed over coke. As practiced at BASF, formamide is heated and split into hydrogen cyanide and water:

$$CH(O)NH_2 \rightarrow HCN + H_2O$$

In the laboratory, small amounts of HCN are produced by the addition of acids to cyanide salts of alkali metals:

$$H^+ + NaCN \rightarrow HCN + Na^+$$

This reaction is sometimes the basis of accidental poisonings because the acid converts a nonvolatile cyanide salt into the gaseous HCN.

Historical methods of production

The demand for cyanides for mining operations in the 1890s was met by George Thomas Beilby, who patented a method to produce hydrogen cyanide by passing ammonia over glowing coal in 1892. This method was used until Hamilton Castner in 1894 developed a synthesis starting from coal, ammonia, and sodium yielding sodium cyanide, which reacts with acid to form gaseous HCN.

Applications

See also: sodium cyanide

HCN is the precursor to sodium cyanide and potassium cyanide, which are used mainly in mining. Via the intermediacy of cyanohydrins, a variety of useful organic compounds are prepared from HCN including the monomer methyl methacrylate, from acetone, the amino acid methionine, via the Strecker synthesis, and the chelating agents EDTA and NTA. Via the hydrocyanation process, HCN is added to butadiene to give adiponitrile, a precursor to Nylon 66.[4]

Occurrence

HCN is obtainable from fruits that have a pit, such as cherries, apricots, apples, and bitter almonds, from which almond oil and flavoring are made. Many of these pits contain small amounts of cyanohydrins such as mandelonitrile and amygdalin, which slowly release hydrogen cyanide.[8][9] One hundred grams of crushed apple seeds can yield about 10 mg of HCN.[*citation needed*] Some millipedes release hydrogen cyanide as a defense mechanism,[10] as do certain insects such as some burnet moths. Hydrogen cyanide is contained in the exhaust of vehicles, in tobacco and wood smoke, and in smoke from burning nitrogen-containing plastics. So-called "bitter" roots of the cassava plant may contain up to 1 gram of HCN per kilogram.[11][12]

HCN and the origin of life

Hydrogen cyanide has been discussed as a precursor to amino acids and nucleic acids. It is possible, for example, that HCN played a part in the origin of life.[13] Although the relationship of these chemical reactions to the origin of life remains speculative, studies in this area have led to discoveries of new pathways to organic compounds derived from condensation of HCN.[14]

HCN in space

See also: Astrochemistry

HCN has been detected in the interstellar medium.[15] Since then, extensive studies have probed formation and destruction pathways of HCN in various environments and examined its use as a tracer for a variety of astronomical species and processes. HCN can be observed from ground-based telescopes through a number of atmospheric windows.[*citation needed*] The $J=1\rightarrow0$, $J=3\rightarrow2$, $J=4\rightarrow3$, and $J=10\rightarrow9$ pure rotational transitions have all been observed.[15][16][17]

HCN is formed in interstellar clouds through one of two major pathways:[18] via a neutral-neutral reaction ($CH_2 + N \rightarrow HCN + H$) and via dissociative recombination ($HCNH^+ + e^- \rightarrow HCN + H$). The dissociative recombination pathway is dominant by 30%; however, the $HCNH^+$ must be in its linear form. Dissociative recombination with its structural isomer, H_2NC^+ produces hydrogen isocyanide (HNC), exclusively.

HCN is destroyed in interstellar clouds through a number of mechanisms depending on the location in the cloud.[18] In photon-dominated regions (PDRs), photodissociation dominates, producing CN ($HCN + \nu \rightarrow CN + H$). At further depths, photodissociation by cosmic rays dominate, producing CN ($HCN + cr \rightarrow CN + H$). In the dark core, two competing mechanisms destroy it, forming HCN^+ and $HCNH^+$ ($HCN + H^+ \rightarrow HCN^+ + H$; $HCN + HCO^+ \rightarrow HCNH^+ + CO$). The reaction with HCO^+ dominates by a factor of ~3.5. HCN has been used to analyze a variety of species and processes in the interstellar medium. It has been suggested as a tracer for dense molecular gas[19][20] and as a tracer of stellar inflow in high-mass star-forming regions[21]. Further, the HNC/HCN ratio has been shown to be an excellent method for distinguishing between PDRs and X-ray-dominated regions (XDRs).[22]

Hydrogen cyanide as a poison and chemical weapon

See also: cyanide poisoning

A hydrogen cyanide concentration of 300 mg/m^3 in air will kill a human within about 10 minutes. It is estimated that hydrogen cyanide at a concentration of 3500 ppm (about 3200 mg/m^3) will kill a human in about 1 minute. The toxicity is caused by the cyanide ion, which halts cellular respiration by inhibiting an enzyme in mitochondria called cytochrome c oxidase.

Hydrogen cyanide absorbed into a carrier for use as a pesticide (under IG Farben's brand name *Cyclone B*, or in German *Zyklon B*, with the **B** standing for *Blausäure*)[23] was most infamously employed by Nazi Germany in the mid-20th century in extermination camps. The same product is currently made in the Czech Republic under the trademark "Uragan D1." Hydrogen cyanide is also the agent used in gas chambers employed in judicial execution in some U.S. states, where it is produced during the execution by the action of sulfuric acid on an egg-sized mass of potassium cyanide.

Hydrogen cyanide is commonly listed amongst chemical warfare agents that cause general poisoning and skin blisters.[24] As a substance listed under Schedule 3 of the Chemical Weapons Convention as a potential weapon which has large-scale industrial uses, manufacturing plants in signatory countries which produce more than 30 tonnes per year must be declared to, and can be inspected by, the Organisation for the Prohibition of Chemical Weapons.

Under the name *prussic acid*, HCN has been used as a killing agent in whaling harpoons.[25]

Hydrogen cyanide gas in air is explosive at concentrations over 5.6%, equivalent to 56000 ppm[26].

External links

- Institut national de recherche et de sécurité (1997). "Cyanure d'hydrogène et solutions aqueuses (http://www.inrs.fr/inrs-pub/inrs01.nsf/inrs01_ftox_view/860430FE710FCFD7C1256CE8004F67CB/$File/ft4.pdf) ". *Fiche toxicologique n° 4*, Paris:INRS, 5pp. (PDF file, *in French*)
- International Chemical Safety Card 0492 (http://www.ilo.org/public/english/protection/safework/cis/products/icsc/dtasht/_icsc04/icsc0492.htm)
- Hydrogen cyanide and cyanides (http://www.inchem.org/documents/cicads/cicads/cicad61.htm) (CICAD 61)
- National Pollutant Inventory: Cyanide compounds fact sheet (http://www.npi.gov.au/database/substance-info/profiles/29.html)
- NIOSH Pocket Guide to Chemical Hazards (http://www.cdc.gov/niosh/npg/npgd0333.html)
- European Chemicals Bureau (http://ecb.jrc.it/)
- Department of health review (http://www.hpa.org.uk/infections/topics_az/deliberate_release/chemicals/cyanide.pdf#search=%22%22dicobalt%20edetate%22%22)
- OSHA: HCN Health Guidelines (http://www.osha.gov/SLTC/healthguidelines/hydrogencyanide/recognition.html)

References

1. ^ Pradyot Patnaik. *Handbook of Inorganic Chemicals*. McGraw-Hill, 2002, ISBN 0070494398
2. ^ "Cyanide, inability to smell" (http://www.ncbi.nlm.nih.gov/entrez/dispomim.cgi?id=304300) . *Online Mendelian Inheritance in Man*. http://www.ncbi.nlm.nih.gov/entrez/dispomim.cgi?id=304300. Retrieved 2010-03-31.
3. ^ Brian T Newbold (1999-11-01). "Claude Louis Berthollet: A Great Chemist in +he french Tradition." (http://www.allbusiness.com/north-america/canada/370855-1.html) . Canadian Chemical News. http://www.allbusiness.com/north-america/canada/370855-1.html. Retrieved 2010-03-31.
4. ^ ***a b*** Ernst Gail, Stephen Gos, Rupprecht Kulzer, Jürgen Lorösch, Andreas Rubo, Manfred Sauer (2004). "Cyano Compounds, Inorganic". *Ullmann's Encyclopedia of Industrial Chemistry*. Verlag, Weinheim: Wiley-VCH. doi:10.1002/14356007.a08 159.pub2 (http://dx.doi.org/10.1002%2F14356007.a08+159.pub2) .
5. ^ The Innovation Group (http://www.the-innovation-group.com/ChemProfiles/Hydrogen%20Cyanide.htm)
6. ^ L. Andrussow (1935). "The catalytic oxydation of ammonia-methane-mixtures to hydrogen cyanide". *Angewandte Chemie* **48**: 593–595.
7. ^ F. Endter (1958). "Die technische Synthese von Cyanwasserstoff aus Methan und Ammoniak ohne Zusatz von Sauerstoff". *Chemie Ingenieur Technik* **30** (5): 281–376. doi:10.1002/cite.330300506 (http://dx.doi.org/10.1002%2Fcite.330300506) .
8. ^ J. Vetter (2000). "Plant cyanogenic glycosides". *Toxicon* **38** (1): 11–36. doi:10.1016/S0041-0101(99)00128-2 (http://dx.doi.org/10.1016%2FS0041-0101%2899%2900128-2) . PMID 10669009 (http://www.ncbi.nlm.nih.gov/pubmed/10669009) .
9. ^ D. A. Jones (1998). "Why are so many food plants cyanogenic?". *Phytochemistry* **47**: 155–162. doi:10.1016/S0031-9422(97)00425-1 (http://dx.doi.org/10.1016%2FS0031-9422%2897%2900425-1) .
10. ^ M. S. Blum, J. P. Woodring (1962). "Secretion of Benzaldehyde and Hydrogen Cyanide by the Millipede *Pachydesmus crassicutis* (Wood)". *Science* **138** (3539): 512–513. doi:10.1126/science.138.3539.512 (http://dx.doi.org/10.1126%2Fscience.138.3539.512) . PMID 17753947 (http://www.ncbi.nlm.nih.gov/pubmed/17753947) .
11. ^ Aregheore E. M, Agunbiade O. O. (1991). "The toxic effects of cassava (manihot esculenta grantz) diets on humans: a review.". *Vet. Hum. Toxicol*. **33** (3): 274–275. PMID 1650055 (http://www.ncbi.nlm.nih.gov/pubmed/1650055) .
12. ^ White W. L. B., Arias-Garzon D. I., McMahon J. M., Sayre R. T. (1998). "Cyanogenesis in Cassava, The Role of Hydroxynitrile Lyase in Root Cyanide Production" (http://www.pubmedcentral.nih.gov/articlerender.fcgi?tool=pmcentrez&artid=35028) . *Plant Physiology* **116** (4): 1219–1225. doi:10.1104/pp.116.4.1219 (http://dx.doi.org/10.1104%2Fpp.116.4.1219) . PMID 9536038 (http://www.ncbi.nlm.nih.gov/pubmed/9536038) .
13. ^ Matthews, C. N. "The HCN World: Establishing Protein-Nucleic Augucid Life via Hydrogen Cyanide Polymers" Cellular Origin and Life in Extreme Habitats and Astrobiology (2004), 6 (Origins : Genesis, Evoluation and Diversity of Life), 121-135.
14. ^ Al-Azmi, A.; Elassar, A.-Z. A.; Booth, B. L. "The Chemistry of Diaminomaleonitrile and its Utility in Heterocyclic Synthesis" Tetrahedron (2003), 59, 2749-2763. CODEN: TETRAB ISSN:0040-4020
15. ^ ***a b*** Snyder, Lewis E.; Buhl, David (1971). "Observations of Radio Emission from Interstellar Hydrogen Cyanide". *Astrophysical Journal* **163**: L47. doi:10.1086/180664 (http://dx.doi.org/10.1086%2F180664) .
16. ^ Bieging, J. H. et al. (2000). "Submillimeter- and Millimeter-Wavelength Observations of SiO and HCN in Circumstellar Envelopes of AGB Stars". *Astrophysical Journal* **543**: 897. doi:10.1086/317129 (http://dx.doi.org/10.1086%2F317129) .
17. ^ Schilke, P. and Menten, K. M. (2003). "Detection of a Second, Strong Sub-millimeter HCN Laser Line toward Carbon Stars". *Astrophysical Journal* **583**: 446. doi:10.1086/345099 (http://dx.doi.org/10.1086%2F345099) .
18. ^ ***a b*** Boger, G. I. and Sternberg, A. (2005). "CN and HCN in Dense Interstellar Clouds". *Astrophysical Journal* **632**: 302. doi:10.1086/432864 (http://dx.doi.org/10.1086%2F432864) .
19. ^ Gao, Y. and Solomon, P. M. (2004). "The Star Formation Rate and Dense Molecular Gas in Galaxies". *Astrophysical Journal* **606**: 271. doi:10.1086/382999 (http://dx.doi.org/10.1086%2F382999) .
20. ^ Gao, Y. and Solomon, P. M. (2004). "HCN Survey of Normal Spiral, Infrared-luminous,

and Ultraluminous Galaxies". *Astrophysical Journal Supplements* **152**: 63. doi:10.1086/383003 (http://dx.doi.org/10.1086%2F383003) .

21. ^ Wu, J. and Evans, N. J. (2003). "Indications of Inflow Motions in Regions Forming Massive Stars". *Astrophysical Journal* **592**: L79. doi:10.1086/377679 (http://dx.doi.org/10.1086%2F377679) .
22. ^ Loenen, A. F. et al. (2007). *Proceedings IAU Symposium* **202**.
23. ^ Dwork, Deborah; van Pelt, Robert Jan (1996). *Auschwitz, 1270 to the present*. Norton. p. 219. ISBN 0393039331.
24. ^ "Hydrogen Cyanide" (http://www.opcw.org/about-chemical-weapons/types-of-chemical-agent/blood-agents/hydrogen-cyanide/) . *Organisation for the Prohibition of Chemical Weapons*. http://www.opcw.org/about-chemical-weapons/types-of-chemical-agent/blood-agents/hydrogen-cyanide/. Retrieved 2009-01-14.
25. ^ Poison Hand Darted Harpoons and Lances (http://www.whalecraft.net/Poison_Irons.html)
26. ^ Documentation for Immediately Dangerous to Life or Health Concentrations (IDLHs) - 74908 (http://www.cdc.gov/Niosh/idlh/74908.html)

Retrieved from "http://en.wikipedia.org/wiki/Hydrogen_cyanide"
Categories: Inorganic compounds | Cyanides | Hydrogen compounds | Blood agents | Fumigants

---