Titanium tetrachloride

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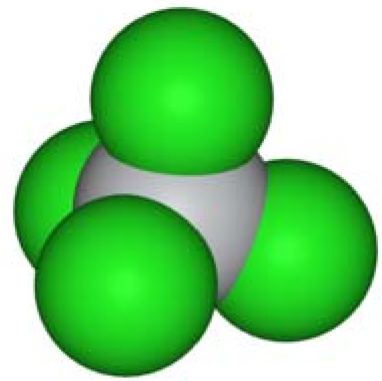
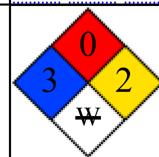
Titanium tetrachloride or **titanium(IV) chloride** is the chemical compound with the formula $TiCl_4$.

$TiCl_4$ is an important intermediate in the production of titanium metal and other titanium compounds. It is an unusual example of a liquid metal halide that is very volatile in air, where it forms spectacular opaque clouds of titanium dioxide (TiO_2) and hydrogen chloride (HCl).

Titanium tetrachloride	
	
General	
Systematic name	Titanium tetrachloride Titanium(IV) chloride
Molecular formula	$TiCl_4$
Molar mass	189.71 g/mol
Appearance	colourless fuming liquid
CAS number	[7550-45-0 (http://www.emolecules.com/cgi-bin/search?t=ss&q=7550-45-0&c=1&v=)]
Properties	
Density and phase	1.730 g/ml, liquid
Solubility in water	Decomposes
Melting point	-24 °C
Boiling point	136.4 °C
Viscosity	? cP at ? °C
Structure	
Molecular shape	Tetrahedral
Dipole moment	zero
Thermodynamic data	
Standard enthalpy	-804.16 kJ/mol

Contents

of formation $\Delta_f H°_{liquid}$	
Standard molar entropy $S°_{liquid}$	221.93 $J \cdot K^{-1} \cdot mol^{-1}$
Safety data	
EU classification	Corrosive
R-phrases	R14, R34
S-phrases	(S1)/(S2), S7/S8, S26, S36/S37/S39, S45
NFPA 704	
Supplementary data page	
Structure and properties	n, ε_r, etc.
Thermodynamic data	Phase behaviour Solid, liquid, gas
Spectral data	UV, IR, NMR, MS
Related compounds	
Other anions	Titanium(IV) fluoride Titanium(IV) bromide Titanium(IV) iodide
Other cations	Zirconium(IV) chloride Hafnium(IV) chloride
Related compounds	Titanium(II) chloride Titanium(III) chloride
Except where noted otherwise, data are given for materials in their standard state (at 25 °C, 100 kPa) Infobox disclaimer and references	

Properties and structure

$TiCl_4$ is a dense, colourless distillable liquid, although crude samples may be yellow or even red-brown. It is one of the rare transition metal chlorides that is in liquid state at room temperature, VCl_4 being another example. This distinctive property arises from the fact that $TiCl_4$ is molecular; that is, each $TiCl_4$ molecule is relatively weakly associated with its neighbours. Most metal chlorides are polymers, where the chloride atoms bridge between the metals. The attraction between the individual $TiCl_4$ molecules is weak, primarily van der Waals forces, and these weak interactions result in low melting and boiling points, similar to those of CCl_4.

$TiCl_4$ is tetrahedral, which is consistent with its description as Ti^{4+} surrounded by four Cl^- ligands. Ti^{4+} has a "closed" electronic shell, with the same number of electrons as the inert gas argon. This configuration leads to highly symmetrical structures, hence the tetrahedral shape of the molecule.

$TiCl_4$ is soluble in toluene and chlorocarbons, as are other non-polar species. Evidence exists that certain arenes form complexes of the type $[(C_6R_6)TiCl_3]^+$. $TiCl_4$ reacts exothermically with donor solvents such as THF to give hexacoordinated adducts.[1] Bulkier ligands (L) give pentacoordinated derivatives $TiCl_4L$.

The main problem with handling $TiCl_4$, aside from its tendency to release corrosive hydrogen chloride, is the formation of titanium oxides and oxychlorides that cement stoppers and syringes.

Production

$TiCl_4$ is produced by the Chloride Process, which involves the reduction of titanium oxide ores, typically ilmenite or rutile, with carbon under flowing chlorine at 900 °C. Impurities are removed by distillation to afford pure $TiCl_4$.

$2FeTiO_3 + 7Cl_2 + 6C \rightarrow 2TiCl_4 + 2FeCl_3 + 6CO$

$TiCl_4$ is inexpensive, thus it is typically purchased for laboratory operations.

Applications

Production of titanium metal

$$TiO_2 + 2Cl_2 + 2C \rightarrow TiCl_4 + 2CO$$

Reduction of $TiCl_4$ using magnesium metal produces titanium metal; this is in fact the final step of the Kroll process.

$$2Mg + TiCl_4 \rightarrow 2MgCl_2(l) + Ti$$

Production of titanium dioxide

Around 90% of the $TiCl_4$ production is used to make pigment; titanium(IV) oxide (TiO_2). Key is the reaction of $TiCl_4$ with water to form hydrochloric acid:

$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$

Or sometimes it is oxidised directly with pure oxygen:

$TiCl_4 + 2O_2 \rightarrow TiO_2 + 2Cl_2$

Smoke-screens

In the past titanium tetrachloride has also been used to create naval smokescreens. When sprayed into the air, $TiCl_4$ rapidly reacts with atmospheric moisture:

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$$

The hydrogen chloride immediately absorbs more water to form tiny droplets of hydrochloric acid, which (depending on humidity) may absorb still more water, to produce large droplets that efficiently scatter light. In addition, the intensely white titanium dioxide is also an efficient light scatterer. Due to the corrosiveness of this smoke, however, $TiCl_4$ is no longer used.

Chemical reactions

Organometallic and inorganic chemistry

$TiCl_4$ adopts similar structures to $TiBr_4$ and TiI_4; the three compounds share many similarities. $TiCl_4$ and $TiBr_4$ react to give mixed halides $TiCl_{4-x}Br_x$, where x = 0, 1, 2, 3, 4. Magnetic resonance measurements also indicate that halide exchange is also rapid between $TiCl_4$ and VCl_4.[2]

$TiCl_4$ is a superb and versatile Lewis acid, as indicated by its tendency to hydrolyze, which implicates the intermediacy of $TiCl_4(H_2O)$. With THF, $TiCl_4$ forms yellow crystals of $TiCl_4(THF)_2$. With Cl^- donors, $TiCl_4$ reacts to form sequentially $[Ti_2Cl_9]^-$, $[Ti_2Cl_{10}]^{2-}$, and $[TiCl_6]^{2-}$.[3] Interestingly, the reaction of chloride ions with $TiCl_4$ depends on the counterion. NBu_4Cl reacts with $TiCl_4$ to give the pentacoordinate complex NBu_4TiCl_5, whereas smaller NEt_4 reacts to give $(NEt_4)_2Ti_2Cl_{10}$. These reactions highlight the influence of electrostatic forces on the structures of compounds with highly ionic bonding.

Much of the extensive organometallic chemistry of titanium starts from $TiCl_4$. Its most important reaction is with sodium cyclopentadienyl to give **titanocene dichloride**, $TiCl_2(C_5H_5)_2$. This compound is used in organic synthesis (Tebbe's reagent). Arenes, such as $C_6(CH_3)_6$ reacts to give $[Ti(C_6(CH_3)_6)Cl_3]^+$, which is a piano-stool complex.[4] This reaction illustrates the extraordinary Lewis acidity of the $TiCl_3^+$ entity, which is derived from $TiCl_4$ using the even stronger chloride-abstracting agent $AlCl_3$.

$TiCl_4$ reacts with four equivalents $LiNMe_2$ to give $Ti(NMe_2)_4$, a yellow, benzene-soluble liquid.[5] This molecule is tetrahedral, with planar nitrogen centers.[6]

Reagent in organic synthesis

It is widely used in organic synthesis as a Lewis acid,[7] for example in the Mukaiyama aldol reaction. Key to this application is the tendency of $TiCl_4$ to interact with aldehydes, RCHO, to give adducts such $(RCHO)TiCl_4OC(H)R$. It is also used in the McMurry reaction in conjunction with Zn, $LiAlH_4$, or another reducing agent in order to join two carbonyls in making a carbon-carbon double bond.

Olefin polymerisation

This compound and many of its derivatives are important precursors to Ziegler-Natta catalysts.

Reduction

Reduction of $TiCl_4$ yields $TiCl_3$. Reduction of $TiCl_4$ with aluminium in THF results in the light-blue THF-adduct $TiCl_3(THF)_3$.

Toxicity and safety considerations

Given the tendency of $TiCl_4$ to hydrolyze, the hazards generally arise from the effect of hydrogen chloride. $TiCl_4$ is a strong Lewis acid, exothermically forming adducts with even weak bases such as THF and explosively with water, again releasing HCl.

References

1. ^ L. E. Manzer (1982). "Tetrahydrofuran Complexes of Selected Early Transition Metals". *Inorganic Synthesis* **21**: 135-40.
2. ^ S. P. Webb, M. S. Gordon (1999). "Intermolecular Self-Interactions of the Titanium Tetrahalides TiX4 (X = F, Cl, Br)". *Journal of the American Chemical Society* **121**: 2552-2560. DOI:S0002-7863(98)03339-3 0.1021/ja983339i S0002-7863(98)03339-3 (http://dx.doi.org/0.1021/ja983339i).
3. ^ C. S. Creaser , J. A. Creighton (1975). "Pentachloro- and Pentabromotitanate(IV) ions". *Journal of the Chemical Society, Dalton Transactions*: 1402-1405. DOI:10.1039/DT9750001402 (http://dx.doi.org/10.1039/DT9750001402).
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5. ^ D. C. Bradey, M. Thomas (1960). "Some Dialkylamino-derivatives of Titanium and Zirconium". *Journal of the Chemical Society*: 3857-3861. DOI:10.1039/JR9600003857 (http://dx.doi.org/10.1039/JR9600003857).
6. ^ M. E. Davie, T. Foerster, S. Parsons, C. Pulham, D. W. H. Rankin, B. A. Smart (2006). "The Crystal Structure of Tetrakis(dimethylamino)titanium(IV)". *Polyhedron* **25**: 923-929. DOI:10.1016/j.poly.2005.10.019 (http://dx.doi.org/10.1016/j.poly.2005.10.019).
7. ^ L.-L. Gundersen, F. Rise, K. Undheim (2004). "Titanium(IV) chloride", *Encyclopedia of Reagents for Organic Synthesis*, L. Paquette, J. Wiley & Sons.

General reading

- Holleman, A. F.; Wiberg, E. "Inorganic Chemistry" Academic Press: San Diego, 2001. ISBN 0-12-352651-5.

- Greenwood, N. N.; Earnshaw, A. (1997). *Chemistry of the Elements*, 2nd Edition, Oxford:Butterworth-Heinemann. ISBN 0-7506-3365-4.

External links

- International Chemical Safety Card 1230 (http://www.ilo.org/public/english/protection/safework/cis/products/icsc/dtasht/_icsc12/icsc1230.htm)
- European Chemicals Bureau (http://ecb.jrc.it/)
- NIST Standard Reference Database (http://webbook.nist.gov/chemistry/)
- Sumitomo Titanium Corporation information sheet (http://www.sumitomocorp.co.jp/o-hitetsu/tetrachl.htm)

- Links to external chemical sources

Categories: Titanium compounds | Chlorides | Metal halides | Reagents for organic chemistry