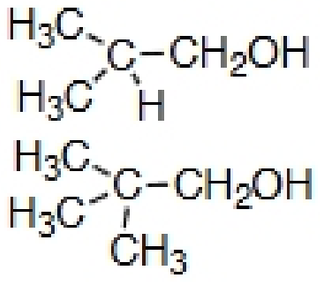
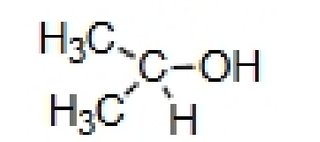
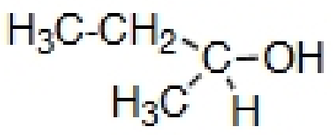
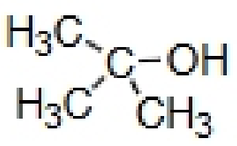
Chapter 13. Alcohols, Diols, and Ethers

Overview: Chemistry and reactions of sp^3 oxygen groups, particularly oxidation of an alcohol, ether formation, and reactions of oxirane (epoxide) groups.

I. What are alcohols, phenols, and ethers?

			IUPAC names	Common names
Alcohols (R-OH)	Primary alcohols (1°-alcohols) pKa ~16-17	CH_3OH	methanol	methyl alcohol
		CH_3CH_2OH	ethanol	ethyl alcohol
		$CH_3CH_2CH_2OH$	1-propanol	*n*-propyl alcohol
			2-methyl-1-propanol	isobutyl alcohol
			2,2-dimethyl-1-propanol	neopentyl alcohol
	Secondary alcohols (2°-alcohols) pKa ~17-18		2-propanol	isopropyl alcohol
			2-butanol	*sec*-butyl alcohol
	Tertiary alcohols (3°-alcohols) pKa ~19		2-methyl-2-propanol	*tert*-butyl alcohol
Phenols (Ph-OH)	pKa ~10-12			
Ethers (R-O-R')		CH_3CH_2-O-CH_2CH_3	diethyl ether	
		Ph-O-CH=CH_2	phenyl vinyl ether	

RO-: alkoxy	CH_3O—	methoxy
	CH_3CH_2O—	ethoxy
ArO-: aryloxy	PhO—	phenoxy

II. Oxidation

Oxidation –

historical use of the term:

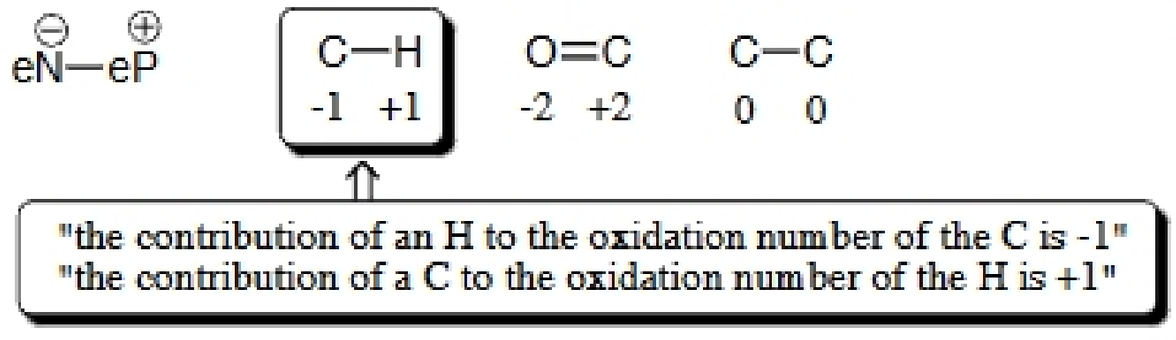
(1) oxide (oxyd/oxyde) – the 'acid' form of an element; e.g., S + air → oxide of S (acid of sulfur)
(2) oxidation or oxidize – to make such an acid, to make the oxide
(3) oxygen – Lavoisier: substance in the air that makes acids; "the bringer of acids" = "oxygen"
(4) oxidation or oxidize – to increase the % oxygen in a substance (reduction: to reduce the % oxygen)

More modern definition:

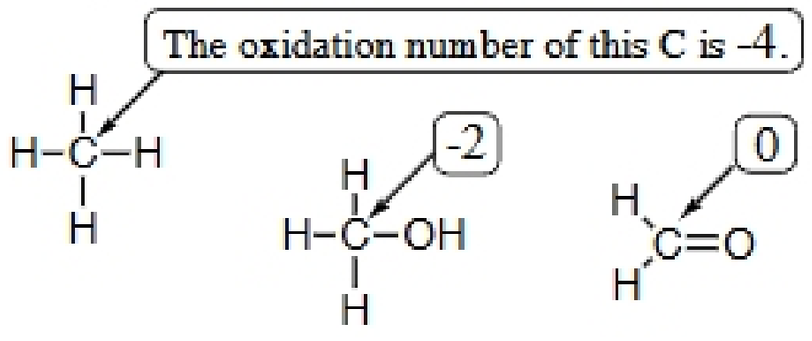
oxidation or oxidize – loss of electrons (coupled with reduction as gain of electrons)

Note: The loss of electrons (oxidation) by one atom or compound must be matched by the gain of electrons (reduction) by another.

III. *Oxidation state* (or *number*) *counting* (see: pp 513-4 of the textbook)

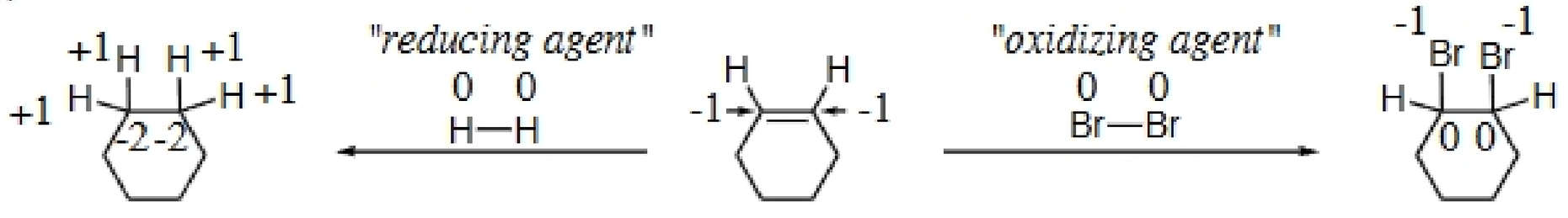


Therefore,

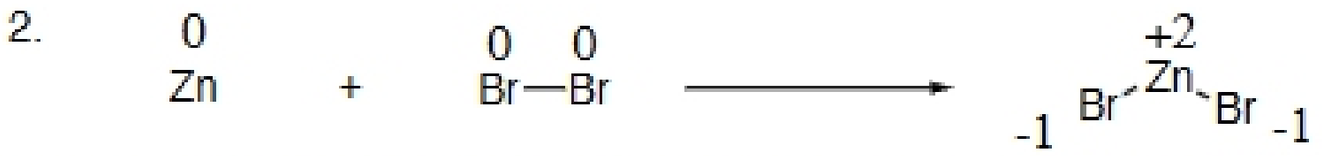


Other examples of oxidation numbers:

1.

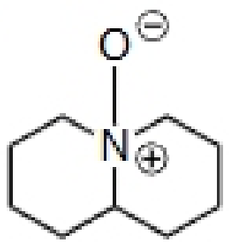


2.



An atom with a formal charge: incorporate its charge # to its oxidation number. Namely, if an atom has a +1 charge, add +1 to its oxidation number.

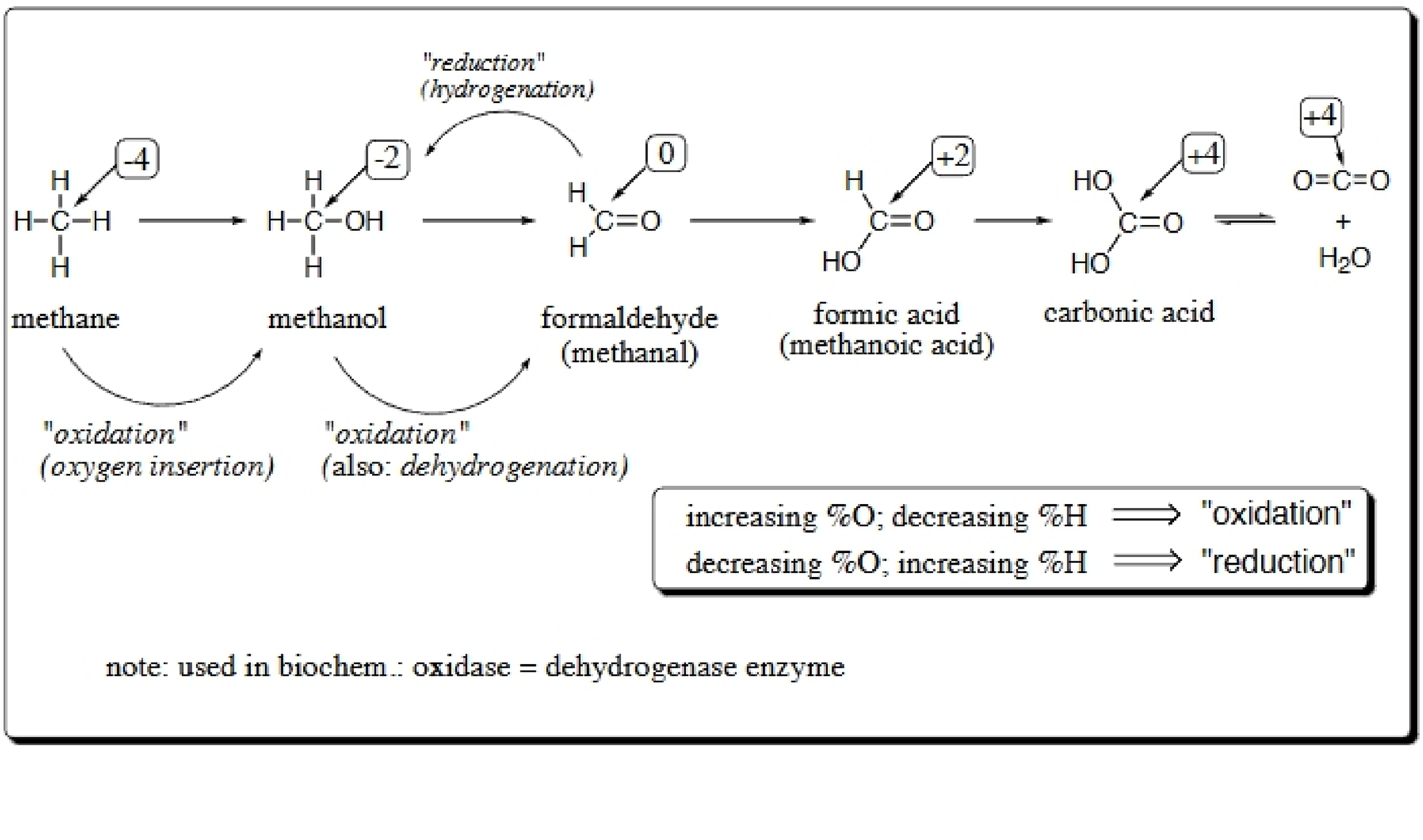
Example:



For N 3 x (- 1) from 3 carbon atoms = -3
+1 from oxygen atom = +1
+1 from the charge = +1
} overall: -1

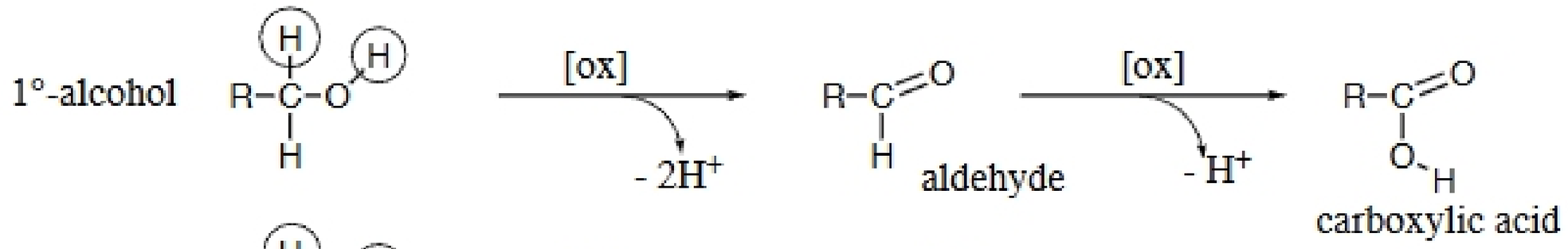
For O -1 from nitrogen atom = -1
-1 from the charge = -1
} overall: -2

Hydrocarbon oxidation-reduction spectrum:



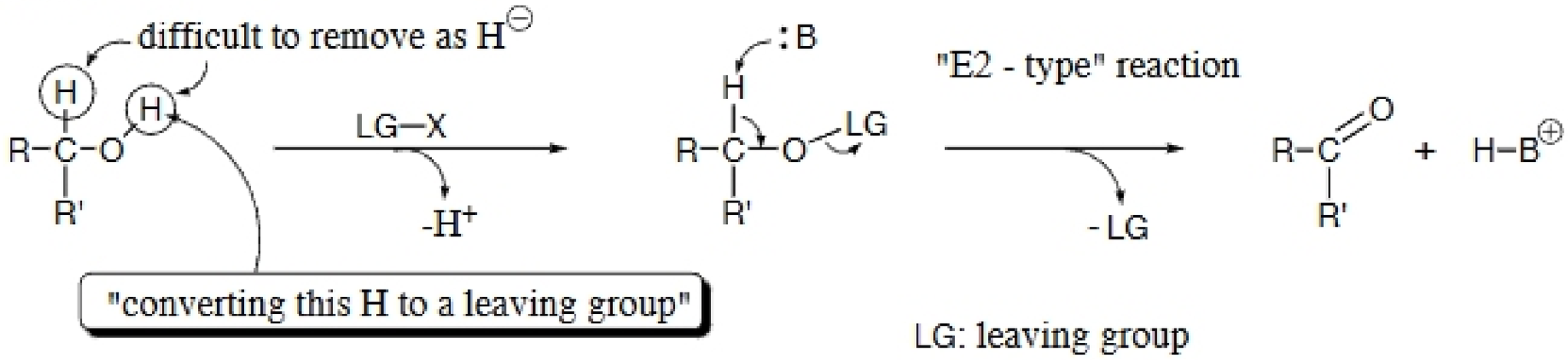
note: used in biochem.: oxidase = dehydrogenase enzyme

IV. Oxidation of alcohols



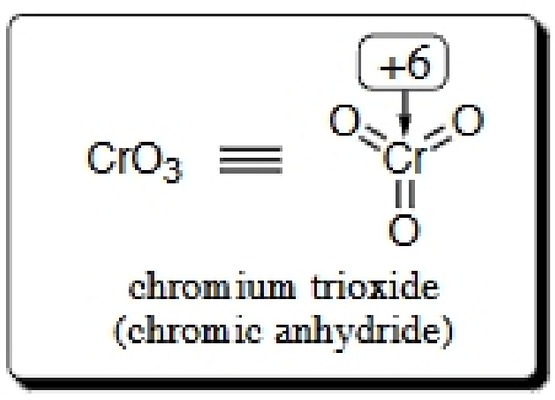
Oxidation methods:

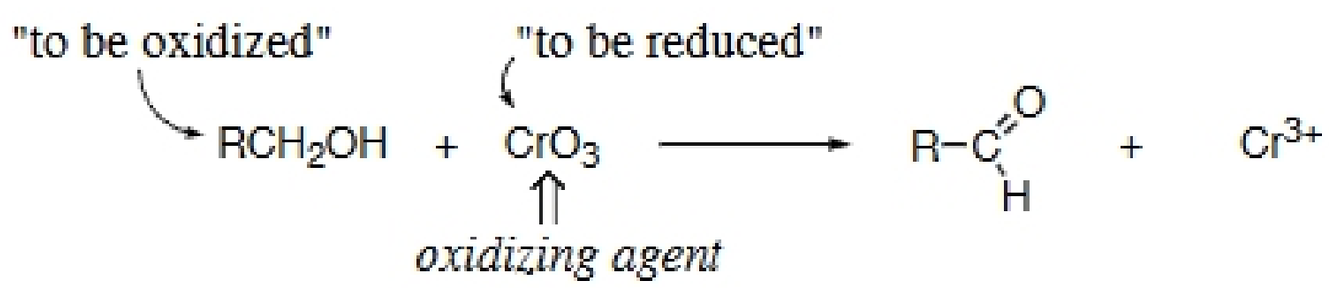
There are hundreds that differ in experimental conditions, but these follow basically the process shown below.



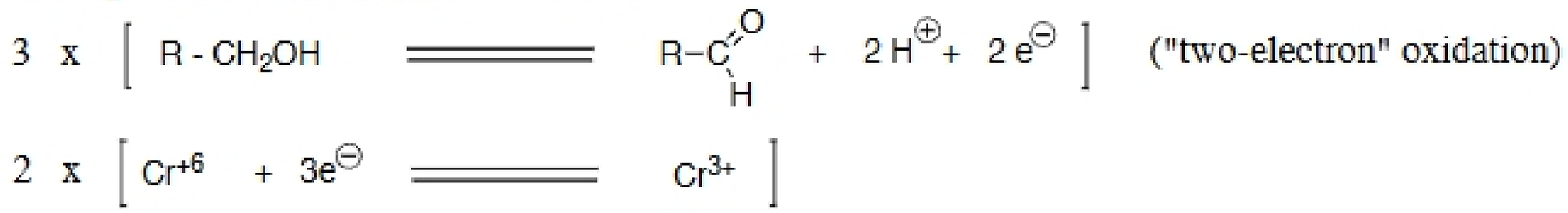
Historically, most common reagents involve high-valency metals.

1. Cr (VI)-based reagents - all Cr(VI) reagents have toxicity problems





Balancing the oxidation-reduction reaction



Overall,