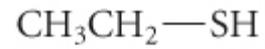


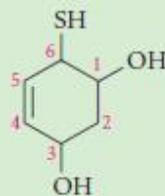
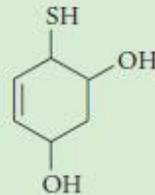
TIOLI: Nomenclatura



etanolo + *tiolo* = **etantiolo**



mercaptano di etile



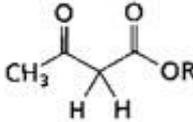
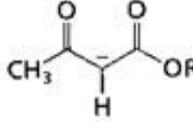
6-mercapto-4-cicloesen-1,3-diolo

TIOLI: proprietà acido-base

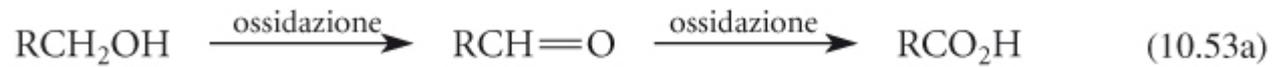


Table 6.3

Acidities of molecules and ions commonly encountered in organic chemistry.^a

| Acid | Conjugate base | pK_a | Acid | Conjugate base | pK_a |
|--|--|--------|---|---|--------|
| HClO ₄ | ClO ₄ ⁻ | -10 | HCN | CN ⁻ | 9.2 |
| HI | I ⁻ | -10 | NH ₄ ⁺ | NH ₃ | 9.2 |
| $\begin{array}{c} \text{+OH} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array}$ | $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array}$ | -10 | ArOH | ArO ⁻ | 10 |
| H ₂ SO ₄ | HSO ₄ ⁻ | -10 | R-CH ₂ NO ₂ | R- $\bar{\text{C}}\text{H}$ -NO ₂ | 10 |
| HBr | Br ⁻ | -9 | RNH ₃ ⁺ | RNH ₂ | 11 |
| HCl | Cl ⁻ | -7 | RSH | RS ⁻ | 11 |
| $\begin{array}{c} \text{+OH} \\ \parallel \\ \text{R}-\text{C}-\text{R} \end{array}$ | $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{R} \end{array}$ | -7 |  |  | 11 |
| ArSO ₃ H | ArSO ₃ ⁻ | -6.5 | CH ₃ OH | CH ₃ O ⁻ | 15.2 |
| $\begin{array}{c} \text{+OH} \\ \parallel \\ \text{R}-\text{C}-\text{OR}' \end{array}$ | $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OR}' \end{array}$ | -6 | H ₂ O | HO ⁻ | 15.7 |
| $\begin{array}{c} \text{H} \\ \\ \text{R}-\text{O}^+-\text{R}' \end{array}$ | R-O-R' | -3.5 | RCH ₂ OH | RCH ₂ O ⁻ | 16 |
| $\begin{array}{c} \text{H} \\ \\ \text{R}-\text{O}^+-\text{H} \end{array}$ | R-O-H | -2 | R ₂ CH-OH | R ₂ CH-O ⁻ | 17 |
| | | | R ₃ C-OH | R ₃ C-O ⁻ | 17 |
| | | | $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{NH}_2 \end{array}$ | $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{NH}^- \end{array}$ | 17 |
| | | | $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array}$ | $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array}$ | 20 |

TIOLI: proprietà redox



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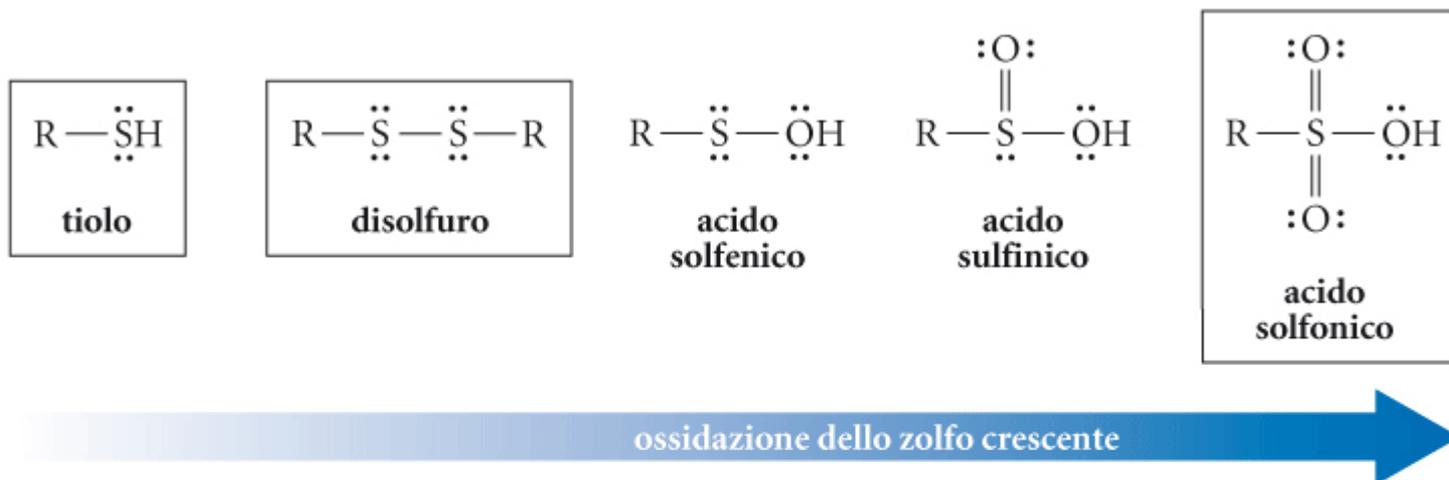
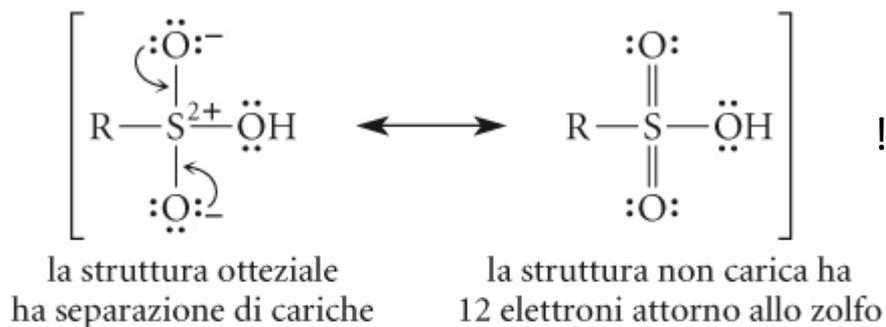
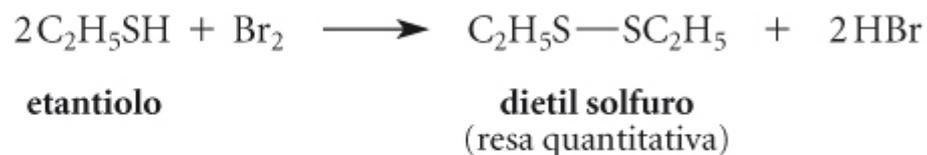
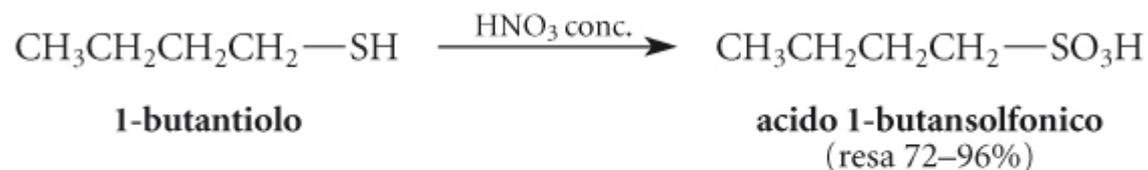


Figura 10.3 L'ossidazione dei tioli può dare diversi prodotti di ossidazione. Fra questi, i disolfuri e gli acidi solfonici (nei riquadri) sono i prodotti più comuni.



! Espansione dell'ottetto per lo zolfo !



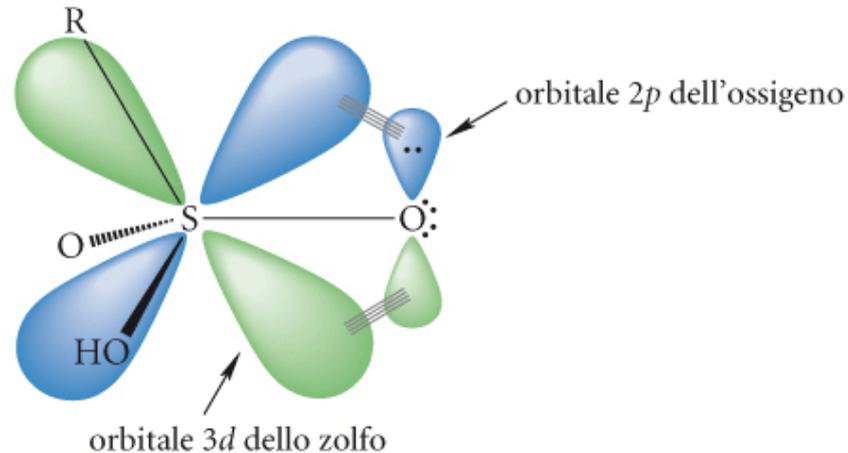
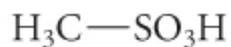
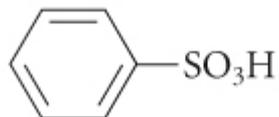


Figura 10.4. Il legame negli stati di ossidazione elevati dello zolfo coinvolge i suoi orbitali $3d$. I lobi positivi e negativi sono mostrati in blu e verde, rispettivamente. Nell'acido solfonico (RSO_3H , Eq. 10.54), una coppia elettronica di non legame sull'ossigeno si sovrappone ad uno dei numerosi orbitali $3d$ dello zolfo. La sovrapposizione è indicata da linee colorate. Nota che questa sovrapposizione è poco efficiente, sia perché gli orbitali hanno dimensioni differenti, sia perché metà dell'orbitale $3d$ dello zolfo punta in una direzione opposta al legame.

! Meno efficiente ancora è la formazione del doppio legame $\text{C}=\text{S}$ che NON può coinvolgere gli orbitali d vuoti dello zolfo !



acido metansolfonico



acido benzensolfonico

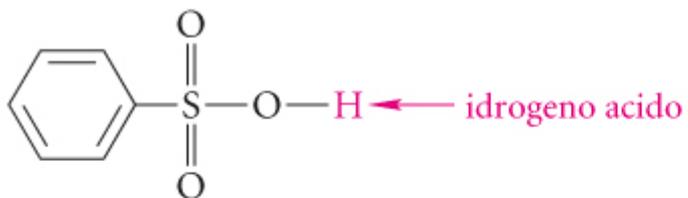


acido *p*-toluensolfonico

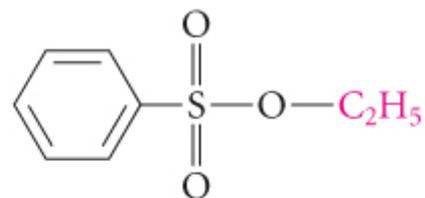


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N.B. protoni acidi!



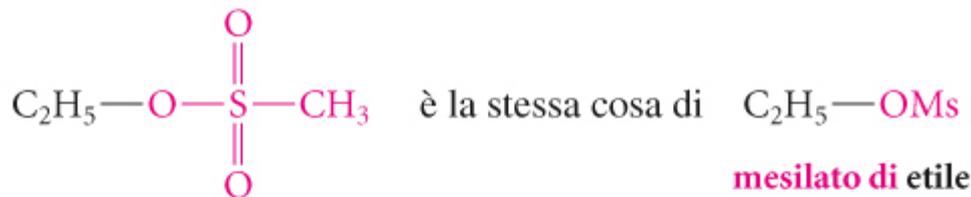
acido benzensolfonico



benzensolfonato di etile
(un estere solfonico)



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metansolfonato di etile



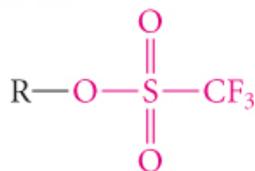
***p*-toluensolfonato di *sec*-butile**

tosilato di *sec*-butile

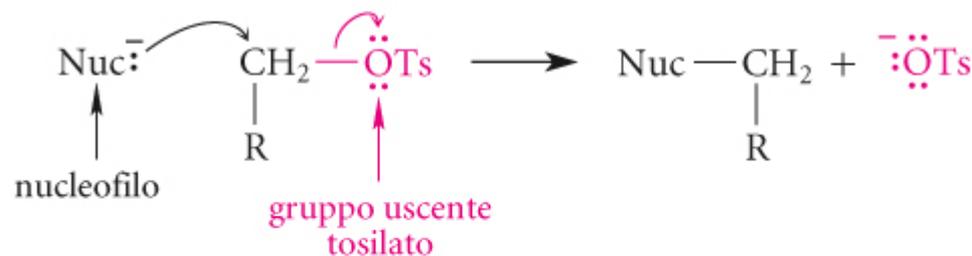
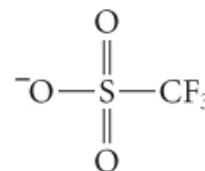


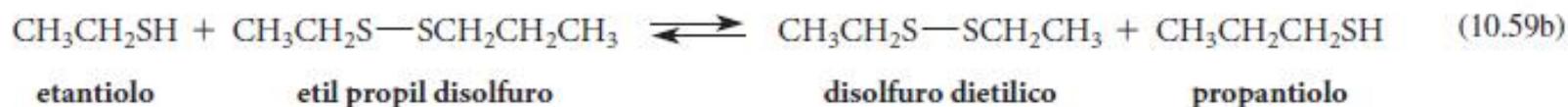
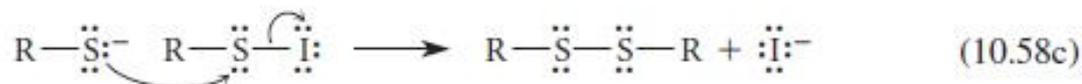
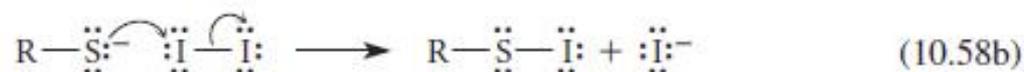
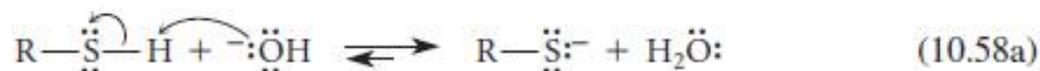
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il gruppo triflato,
 un gruppo uscente molto reattivo

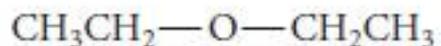


$\text{R}-\text{OTf}$
 abbreviazione per
 l'estere triflato

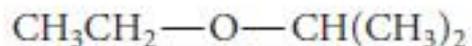




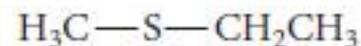
SOLFURI: Nomenclatura



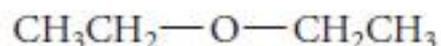
dietil etere



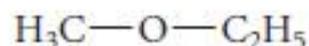
etil isopropil etere



etil metil solfuro



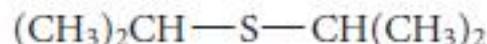
dietil etere
(o anche etere etilico
o semplicemente etere)



etil metil etere



etil metil solfuro
(o anche etil metil tioetere)

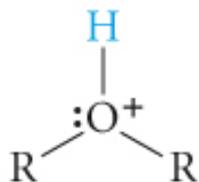


diisopropil solfuro

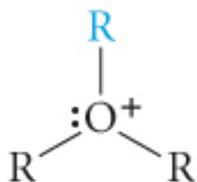


2-etossi-5-metilesano

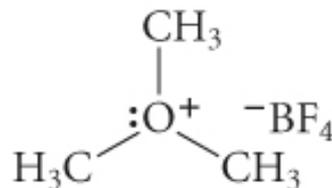
I Sali di SOLFONIO in Biochimica



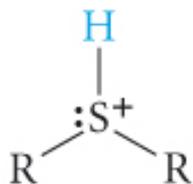
un etere
protonato



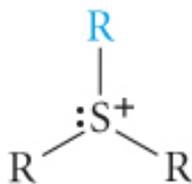
uno ione di
trialchilossonio



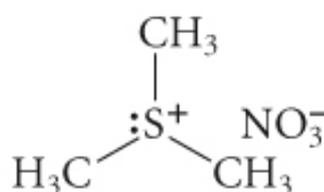
**tetrafluoroborato
trimetilossonio**
(un sale di ossonio)



un solfuro
protonato

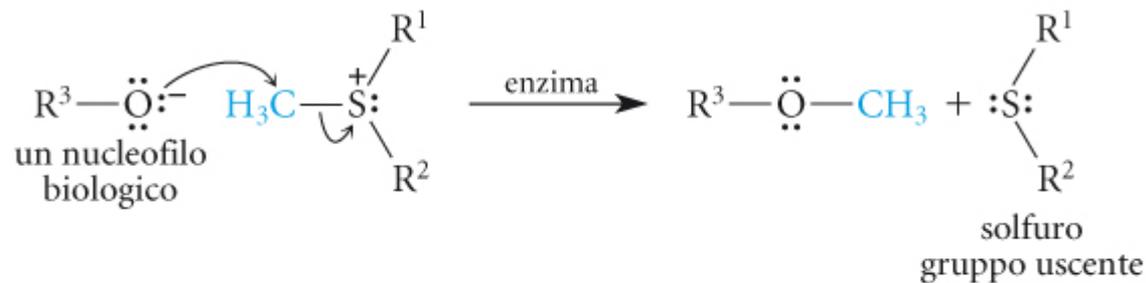
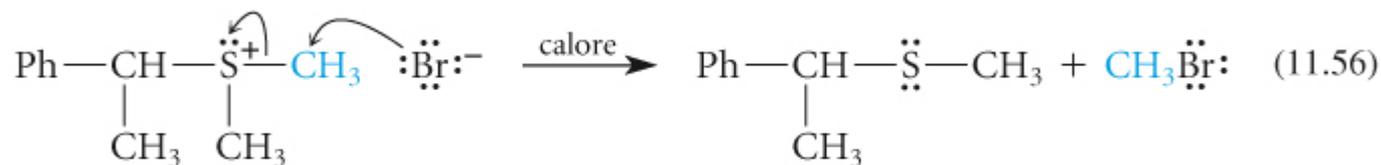


uno ione di
trialchilsolfonio



**nitrate di
trimetilsolfonio**
(un sale di solfonio)





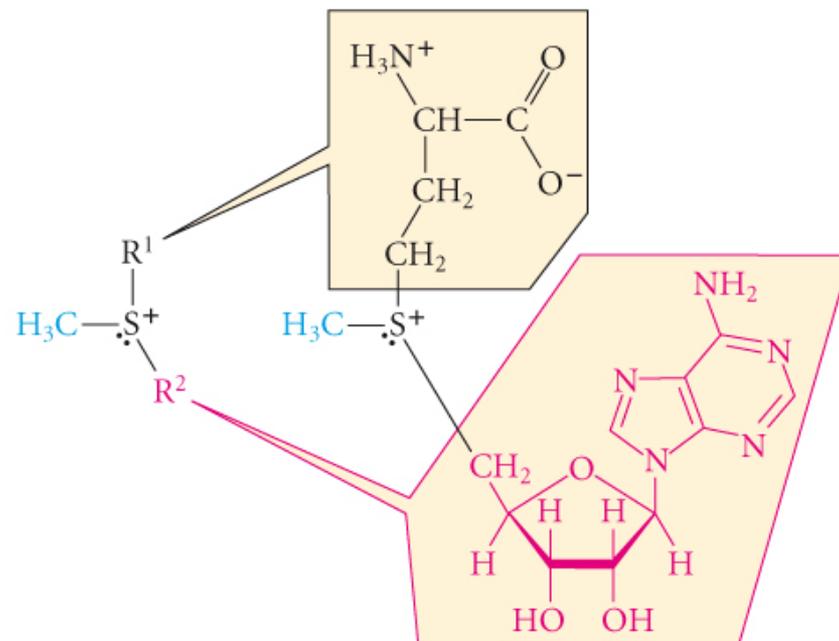
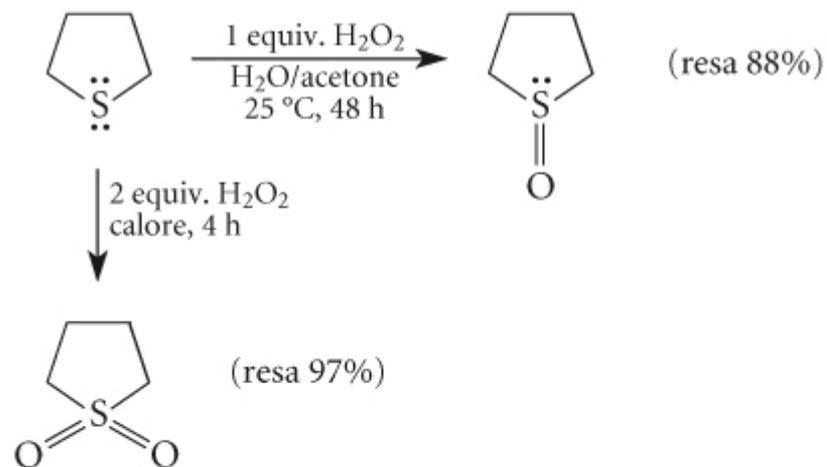
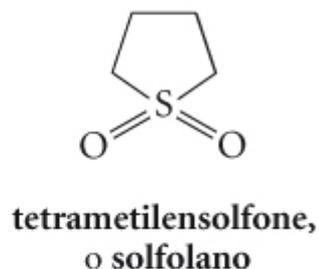
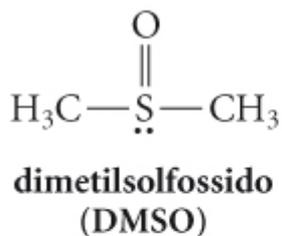
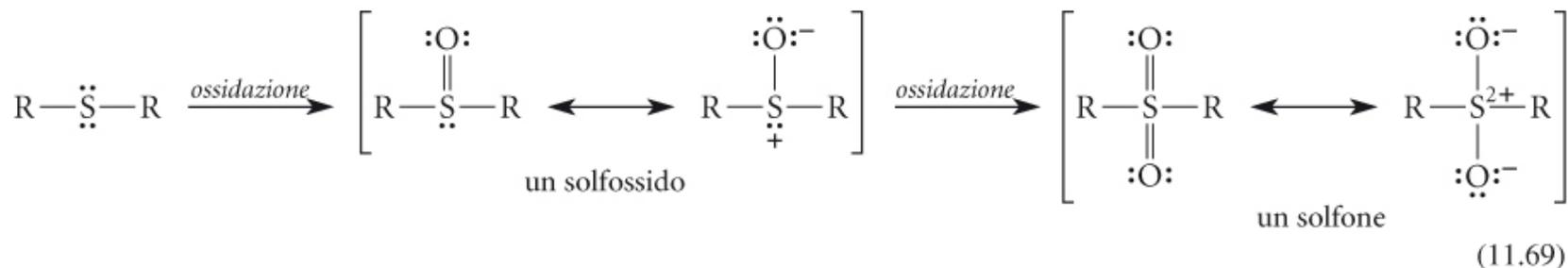


Figura 11.1 S-Adenosilmetionina (SAM). Le parti della struttura racchiuse nei riquadri sono abbreviate con R¹ e con R² nel testo.

SOLFURI: Reattività REDOX



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