THE CHEMISTRY OF BIOLOGICAL NITROGEN FIXATION

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CHEMISTRY CASSETTES

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USING THIS CHEMISTRY CASSETTE

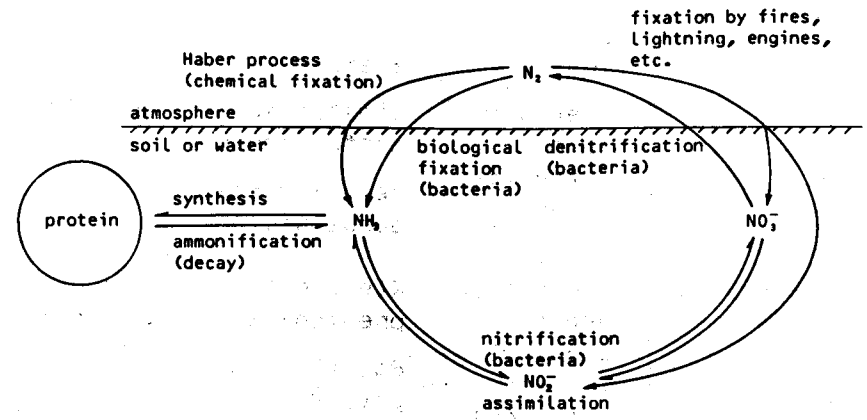
Please read this before you use the cassette.

This Chemistry Cassette learning programme consists of an audio-cassette and this workbook. The two are designed to be used together so always have the workbook with you as you work through the cassette.

You will see that material in the workbook has been divided into numbered 'frames', each of which contains diagrams, tables, equations, etc. Whenever Dr Richards wants to refer you to any of this material he will give you the appropriate frame number.

The programme has been carefully designed for individual, self-paced learning, and you can work through it at a rate related to your own needs and understanding. Switch off the tape player whenever you want to think, to write some notes, or to answer a question. Use the rewind control to revise or repeat material that you may not fully understand on a first hearing. Always have pen and paper with you so that you can make notes to supplement or amplify the material contained in this workbook - this will enable you to build up a detailed set of personal notes which will serve as your own authoritative guide to the subject.

1 THE BIOLOGICAL NITROGEN CYCLE



2 FIXATION PROCESSES

Oxidation via fires, etc. — tonnes/year

$$N_2 \xrightarrow{O_2} \begin{cases} NO_2^- \\ NO_3^- \end{cases} \qquad 5\times10^7$$

Industrial (Haber process)

$$\left.\begin{matrix}\text{Natural gas}\\ \text{Oil}\\ \text{Coal}\end{matrix}\right\} \rightarrow 3H_2 + N_2 \xrightarrow[400^\circ - 500^\circ,\ 80\text{–}350\ \text{atm}]{\text{Fe catalyst}} 2NH_3 \qquad 6\times10^7$$

Biological

$$N_2 \xrightarrow[H_2O,\ \text{sunlight}]{\text{bacteria}} 2NH_3 \qquad 9\times10^7$$

Total fixed N for agriculture 20×10^7

3 NITROGEN-FIXING BACTERIA

	Type	Example	Occurrence
Free-living	anaerobic (cannot metabolise oxygen)	Clostridium pasteurianum	anaerobic soils
		Desulfovibrio desulfuricans	
	facultative (aerobic when not fixing nitrogen)	Klebsiella pneumoniae	aerobic and anaerobic soils, water
		Bacillus polymyxa	
	aerobic (can metabolise oxygen)	Azotobacter chroococcum	aerobic soils
		Derxia gummosa	
Symbiotic (legumes)		Rhizobium	root nodules of legumes, peas, beans, etc.

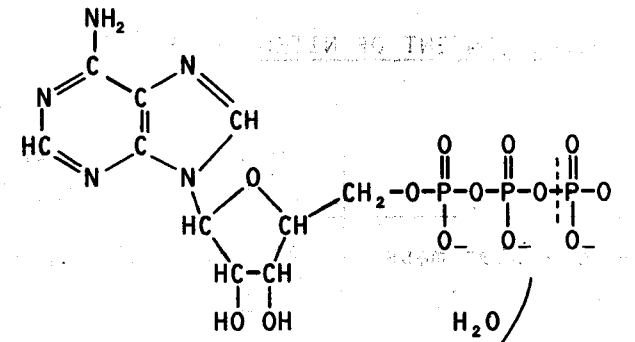
4 BIOLOGICAL REDUCTION OF DINITROGEN

$$N_2 + 6H^+ + 6e^- \xrightarrow[\text{enzyme + energy}]{\text{nitrogenase}} 2NH_3$$

1 atmos.
∿ 20°

In principle, adenosine triphosphate (ATP) hydrolysis provides the energy for the process.

ATP



$ADP + PO_4^{3-} + 2H^+$

5 SUBSTRATES OF NITROGENASE

Substrate	Products of reduction
dinitrogen (N_2)	$2NH_3$
proton (H^+)	$\frac{1}{2}H_2$
methyl isocyanide ($CH_3N{\equiv}C$)	$CH_3NH_2 + CH_4$ (+ C_2H_2 and C_2H_4 in low yield)
ethyne ($HC{\equiv}CH$)	$H_2C{=}CH_2$
cyanide ion ($C{\equiv}N^-$)	$CH_4 + NH_3$
carbon monoxide ($C{\equiv}O$)	not reduced

6 METAL CONTENT OF NITROGENASE PROTEINS

	Mo-Fe protein	Fe protein
relative molecular mass	220 000	55 000 - 70 000
Mo content†	2	0
Fe content†	18-32	4
sulphide ion content†	18-32	4

†atoms per molecular unit

7 SIMPLIFIED MECHANISM OF NITROGENASE ACTION

$Na_2S_2O_4$ (sodium dithionite, source of electrons)

+

Mg^{2+} (ATP activator)

+

ATP

+

Fe protein

N_2

+

MoFe protein

Fe protein$^-$ MgATP | MoFe protein N_2

protein-protein | electron transfer

Fe protein Mg{ATP / ADP} | MoFe$^-$ protein N_2

$6H^+$

five more electron transfer steps

Fe protein

MoFe protein

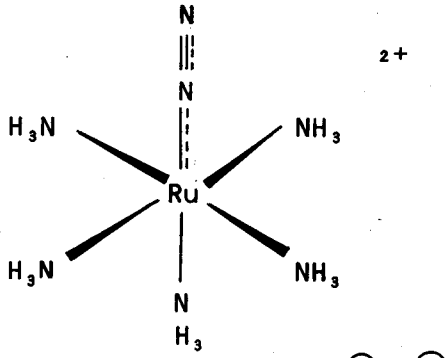
$2NH_3$

+ MgADP + PO_4^{3-}

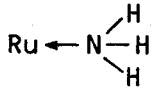
$$ATP \xrightarrow{H_2O} ADP + PO_4^{3-} + \text{energy}$$

8 A DINITROGEN COMPLEX OF RUTHENIUM

(a)

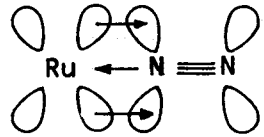


(b)



σ-bonding only, by donation of lone pair of electrons from N to Ru.

(c)

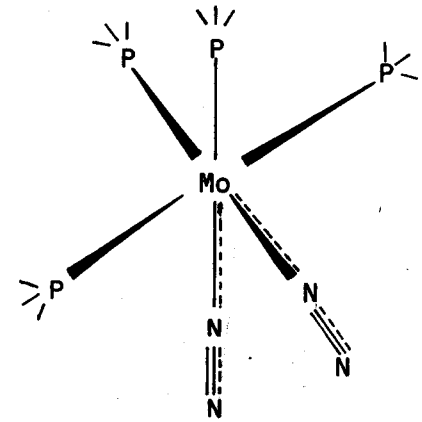


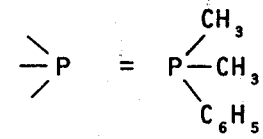
σ-bonding +
π-bonding

Ru⋮⋮N≡N

Delocalised bonding. σ-lone pair donated from N to Ru, plus π-donation from filled d-orbitals of Ru to vacant π^*-orbitals on N_2

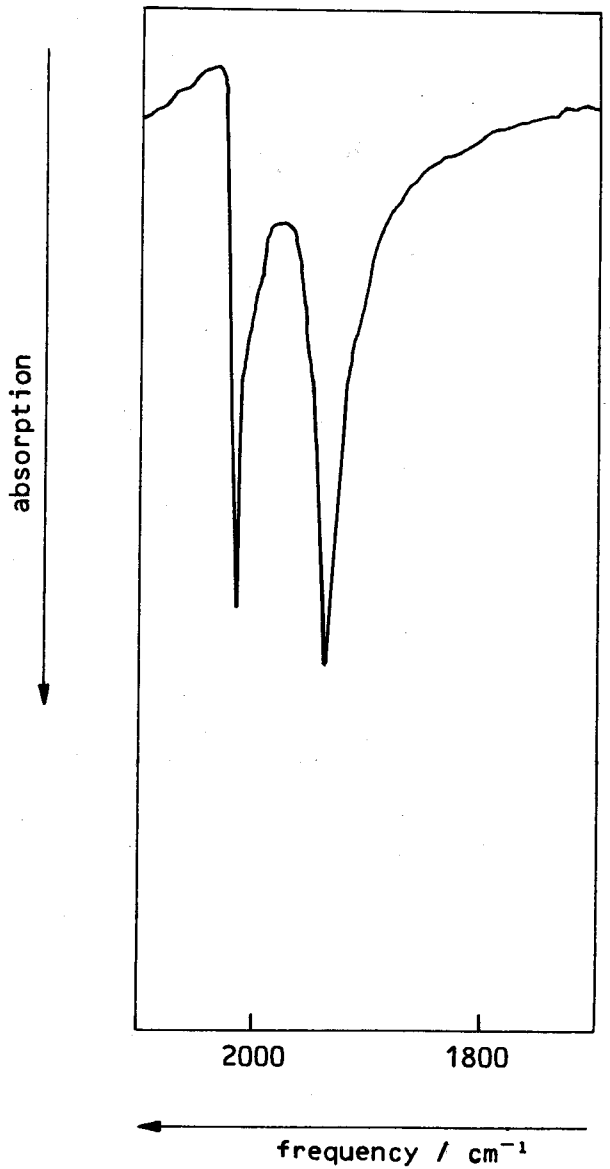
9 A DINITROGEN COMPLEX OF MOLYBDENUM





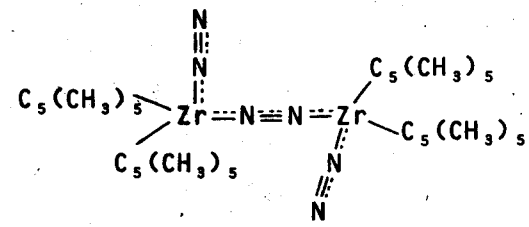
10

INFRA-RED ABSORPTION SPECTRUM OF $[Mo(N_2)_2(PMe_2Ph)_4]$ IN THE DINITROGEN REGION



11

STRUCTURE OF A BINUCLEAR DINITROGEN COMPLEX



12

SPECTROSCOPIC DATA AND BOND DISTANCES FOR DINITROGEN AND ITS COMPLEXES

Compound	Frequency of N_2 vibration (cm^{-1}) IR	Raman	N-N distance (Å)
N_2	-	2331	1.0976
$[Mo(N_2)_2\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2]$†	1979	-	1.118
$[\{Zr(C_5(CH_3)_5)_2(N_2)\}_2(N_2)]$	2006 *	-	1.116*
	2041 *		
	1556¤¶		1.182¤

† a very similar complex to that of frame 9.
* end-on
¤ bridging
¶ weak absorption

13 DINITROGEN REDUCING SYSTEMS

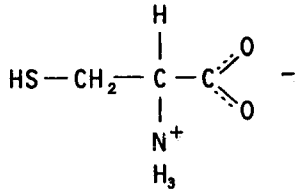
Complex	Redg. agent	P_{N_2} /atm	T /°C	Product	Yield†
(a) $MoOCl_3$*	$TiCl_3$	100	85	N_2H_4	2.0
$VSO_4.7H_2O$*	-	100	20	N_2H_4	0.22
$VSO_4.7H_2O$¤	-	1	25	NH_3	0.16
(b) $Na_2[Mo_2O_4(cys)_2]$¶	$NaBH_4$	1	27	NH_3	0.04
$K_2[MoO(CN)_4(H_2O)]$	$NaBH_4$	1	27	NH_3 N_2H_4	0.29 0.029

† yield expressed as mols NH_3 or N_2H_4 per metal atom.
* with $MgCl_2$ and KOH in aqueous methanol.
¤ with added catechol at pH ∿10.
¶ cys = $[SCH_2CH(NH_2)CO_2]^{2-}$ from cysteine (frame 14).

(a) = systems developed by Shilov.

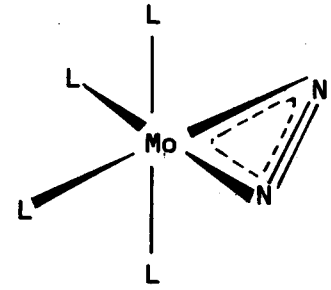
(b) = systems developed by Schrauzer.

14 THE CYSTEINE MOLECULE



15 SIDEWAYS-BOUND DINITROGEN

A.



L = other ligands

B. $M_L \equiv N \equiv N \equiv M_L$

M_L = Mo or V atoms plus attached ligands, which bind to Mo and V via oxygen atoms.

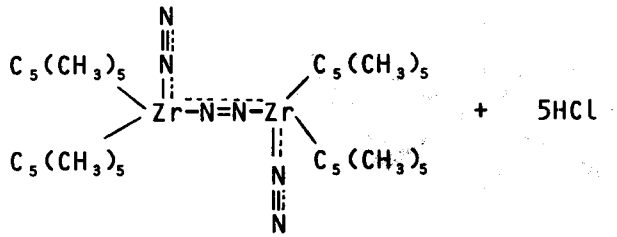
16 PRODUCTION OF AMMONIA FROM A MONONUCLEAR COMPLEX

$$[M(N_2)_2\{P(CH_3)_2C_6H_5\}_4] \xrightarrow[CH_3OH]{H_2SO_4} xNH_3 + yN_2 + \text{oxidised metal products}$$

M = W, x = 2, y = 1
M = Mo, x = 1, y = $^3/_2$

17

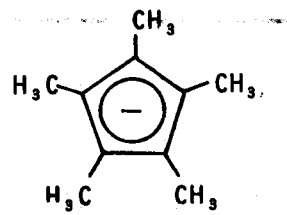
PRODUCTION OF HYDRAZINE FROM A BINUCLEAR COMPLEX



toluene | −80°C

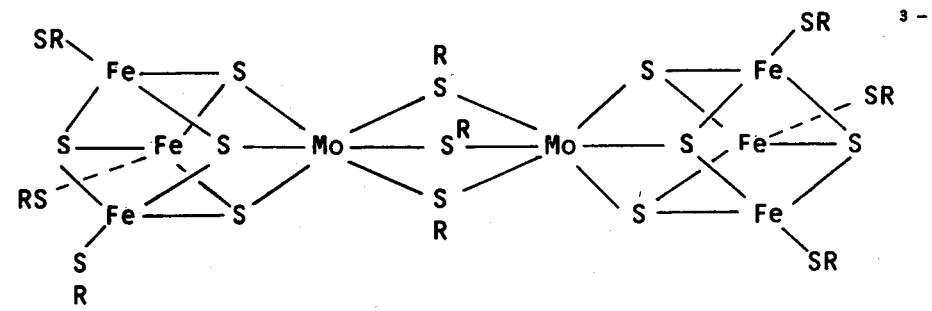
$2[Zr\{C_5(CH_3)_5\}_2Cl_2] + 2N_2 + N_2H_4.HCl$

$C_5(CH_3)_5$ =



18

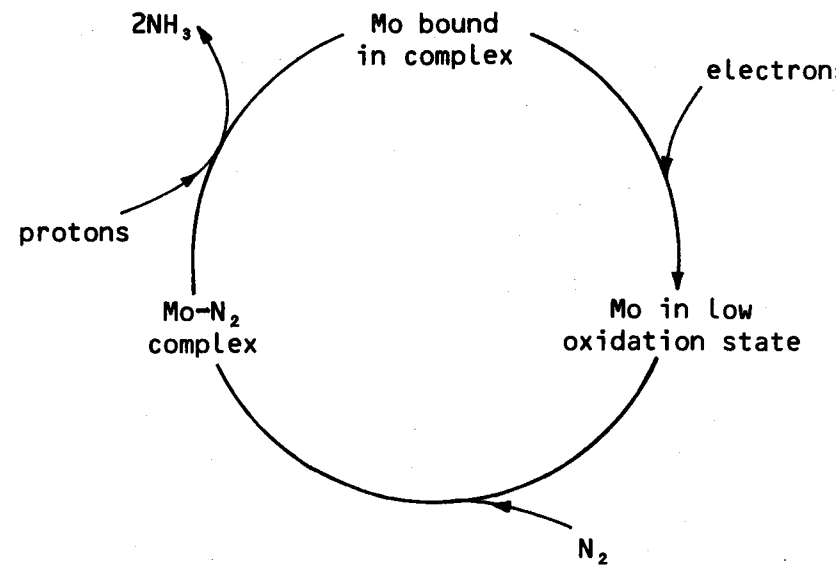
A COMPLEX CONTAINING MOLYBDENUM, IRON AND SULPHIDE IN A 'CLUSTER'

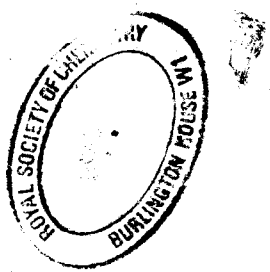


R = C_6H_5 or C_2H_5

19

CYCLIC PROCESS FOR THE REDUCTION OF DINITROGEN





FURTHER READING

J R Postgate: Nitrogen Fixation (Studies in Biology No. 92), Arnold, London, 1978
A general coverage of biological aspects.

S P S Andrews: Haber Process, Education in Chemistry 1978, 15, 115.
A brief summary of the Haber process.

R L Richards: Nitrogen Fixation, Education in Chemistry, 1979, 16, 66.
A brief summary of chemical aspects.

J Chatt, L M Camara Pina and R L Richards (editors), New Trends in the Chemistry of Nitrogen Fixation, Academic Press, London, 1980.
A comprehensive account of chemical aspects.