Catalytic Fixation of Nitrogen

By M. E. VOLPIN,* M. A. ILATOVSKAYA, L. V. KOSYAKOVA, and V. B. SHUR
(*Institute of Organo-element Compounds, Academy of Sciences of the U.S.S.R., Vavilova Street, 28, Moscow, U.S.S.R.*)

A GREAT number of systems based on transition-metal compounds and reducing agents react with molecular nitrogen[1] to form nitride-like compounds which yield ammonia on hydrolysis.

However, none of these systems is catalytic. All attempts to attain catalytic nitrogen fixation, by increasing the amount of reducing agents and prolonging the reaction time, *etc.*, failed and in no case did the yield of ammonia exceed 1—2 moles per mole of the transition-metal compound.

The noncatalytic character of these reactions may well be due to the transition-metal compound, responsible for nitrogen activation, being in some cases unstable and rapidly removed by side reactions.

Another, more general, reason may be due to the formation of strong nitride-like bonds between the transition-metal and the nitrogen atoms during the molecular nitrogen reduction. This prevents the regeneration of active transition-metal compound and thus makes the reaction noncatalytic.

Since nitride bonds are known sometimes to split under the action of acids, we suggested that a nitrogen-fixing system could become catalytic when the nitrogen reaction is carried out in the presence of acids. However, as the protic acids destroy nitrogen-fixing systems, we attempted to achieve the catalytic fixation of nitrogen by using aprotic acids.

We have studied the nitrogen reactions with systems consisting of aluminium, aluminium halides, and transition-metal compounds, such as $TiCl_4$, $Ti(OR)_4$, $ZrCl_4$, $CrCl_3$, $MoCl_5$, WCl_6, $MnCl_2$, $FeBr_3$, $FeCl_3$, $NiBr_2$, and $CoCl_2$, *etc.* These systems which are of considerable reductive power include the aprotic acid, and have been widely used for the synthesis of arenic[2] and carbonyl[3] complexes of transition-metals and also the polymerization and cyclization of olefins. We have found that by using these systems catalytic nitrogen fixation can also be achieved.

Thus nitrogen is reduced by a mixture of $TiCl_4$, Al, and $AlBr_3$ at a temperature $>50°$ to form products with metal–nitrogen bonds, which yield ammonia on hydrolysis. The reaction can be carried out in the presence of solvent (*e.g.* benzene) as well as without any added solvent, *i.e.* in molten $AlBr_3$.

The nitrogen reaction was of a catalytic character. With increasing amounts of Al and $AlBr_3$ the ammonia yield increases up to 200 or more moles per mole of initial $TiCl_4$ (*cf.* Table).

Since, in the absence of $TiCl_4$, neither aluminium, nor its mixture with $AlBr_3$, reacts with nitrogen, the titanium compound is a catalyst of the nitrogen reduction with aluminium.† On heating TiX with a mixture of Al and AlX_3 ($X = Cl$ or Br) in benzene, Ti^{IV} is reduced to Ti^{II} and the stable complex $C_6H_6,TiX_2,2AlX_3$ is formed.[4] This divalent titanium compound seemed to be the real catalyst of nitrogen fixation when the reaction is carried out in the presence of benzene.‡

Indeed, we have found that on heating (130°) the mixture of Al, $AlBr_3$, and a catalytic amount of $C_6H_6,TiCl_2,2,AlCl_3$ (in molar ratio of Al : $AlBr_3$: Ti-complex $= 150 : 250 : 1$) with nitrogen, the latter is reduced to form 115 moles of ammonia per mole of titanium complex upon hydrolysis (yield $\simeq 80\%$ consumption of aluminium).

In the absence of Al and $AlBr_3$, the complex

---

† Aluminium can be replaced by other reducing agents (*e.g.* $LiAlH_4$) in this catalytic reaction.

‡ With reaction carried out in the absence of C_6H_6, a similar complex, but without benzene ligand, can act as a catalyst.

Nitrogen fixation by the system of $TiCl_4$ + Al + $AlBr_3$‡

Molar ratio $TiCl_4 : Al : AlBr_3$	C_6H_6, moles per mole of $TiCl_4$	Reaction time (hr.)	Ammonia yield (moles per mole of $TiCl_4$)
1 : 2 : 1	9	8	0·80
1 : 6 : 1	9	8	0·84
1 : 6 : 2	9	8	1·25
1 : 12 : 0	9	8	0·03
1 : 12 : 16	9	8	4·2
1 : 12 : 16	0	30	6·44
1 : 12 : 16	18	30	6·65
1 : 12 : 33	0	30	10·7
1 : 150 : 200	0	30	95
1 : 600 : 1000	0	30	284

‡ At the temperature 130°; nitrogen pressure ~100 atmos.

$C_6H_6,TiCl_2,2AlCl_3$ reacts with nitrogen at 130° to form a compound, whose elemental analysis is close to that for $C_6H_6(TiCl_2,2AlCl_3)_3N$. This compound hydrolysed to give a stoicheiometric yield of ammonia.

(*Received, May 27th,* 1968; *Com.* 692.)

[1] M. E. Volpin and V. B. Shur, *Doklady Akad. Nauk S.S.S.R.*, 1964, **156**, 1102; *Vestnik Akad. Nauk S.S.S.R.*, 1965, No. 1, 51; *Zhur. Vsesoy. Khim. obsh. im. D. I. Mendeleeva*, 1967, **12**, 31; *Nature*, 1966, **209**, 1236; G. Henrici-Olivé and S. Olivé, *Angew. Chem. Internat. Edn.*, 1967, **6**, **873**; E. E. van Tamelen, G. Boche, S. W. Ela, and R. B. Fechter, *J. Amer. Chem. Soc.*, 1967, **89**, 5707.

[2] E. O. Fischer, W. Hafner, *Z. Naturforsch.*, 1955, **10b**, 665.

[2] E. O. Fischer, W. Hafner, K. Ofele, *Chem. Ber.*, 1959, **92**, 3040.

[4] G. Natta, G. Mazzanti, and G. Pregaglia, *Gazzetta*, 1959, **89**, 2065.

[5] H. Martin and F. Vohwinkel, *Chem. Ber.*, 1961, **94**, 2416.